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ENVIRO

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Problem

Spills

PHOSPHORIC ACID

March 1985

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The report has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

EnviroTIPS manuals are available from:

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PHOSPHORIC ACID

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

March 1985

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

PHOSPHORIC ACID (H_3PO_4)

Colourless to amber, thick liquid or solid, odourless

SYNONYMS

Orthophosphoric Acid, Acide Phosphorique (Fr.)

IDENTIFICATION NUMBERS

UN. No. 1805; CAS No. 7664-38-2; OHM-TADS No. 7216852; STCC No. 4930248

GRADES & PURITIES

Technical: 75, 80, 85, 105, 115 percent H_3PO_4

Food: 75, 80, 85 percent H_3PO_4

Pure: 85, 90 percent H_3PO_4

Fertilizer: 72 percent H_3PO_4 (Generally available from 33 to 115 percent H_3PO_4)

IMMEDIATE CONCERNS

Fire: Not combustible

Human Health: Low toxicity, corrosive by ingestion and contact

Environmental: Harmful to aquatic life due to pH reduction

PHYSICAL PROPERTY DATA

	75 percent	80 percent	85 percent
State: (15°C, 1 atm):	liquid	liquid	solid
Boiling Point:	158°C	147°C	158°C
Melting Point:	-17.5°C	4.6°C	21°C
Flammability:	not combustible	not combustible	not combustible
Specific Gravity (25°/4°C):	1.574	1.628	1.685
Solubility (in water):	miscible	miscible	miscible
Behaviour (in water):	sinks and mixes, with mild evolution of heat		
Odour Threshold:	odourless	odourless	odourless

ENVIRONMENTAL CONCERNS

The toxicity of phosphoric acid is largely due to increased acidity (to pH 5 or less). Phosphate concentrations over 0.01 mg/L may stimulate undesirable algal growth.

HUMAN HEALTH

TLV•: 1 mg/m^3
IDLH: not established

Exposure Effects

Inhalation (of mist): Irritation to mucous membranes, coughing

Contact: (skin) Irritation and burns; (eyes) irritation, conjunctivitis and burns

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE". Notify manufacturer. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible, most fire-extinguishing agents are compatible. Cool fire-exposed containers with water.

COUNTERMEASURES

Emergency Control Procedures in/on

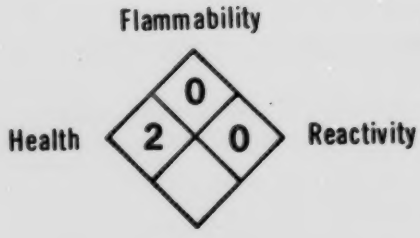
Soil: Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Absorb residual liquid with natural or synthetic sorbents. Neutralize contaminated soil with lime or sodium bicarbonate.

Water: Contain by damming, water diversion or natural barriers. Neutralize contaminated water with lime.

NAS HAZARD RATING

Category	Rating
Fire	0
Health	
Vapour Irritant	0
Liquid or Solid Irritant	3
Poison	1
Water Pollution	
Human Toxicity	2
Aquatic Toxicity	3
Aesthetic Effect	2
Reactivity	
Other Chemicals	3
Water	0
Self-reaction	0

NFPA HAZARD CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

	100%	85%	80%	75%
Physical State Properties				
Appearance	Syrupy amber liquid or white to amber solid (Erco PD)			
Usual shipping state	Not commercially available	Liquid	Liquid	Liquid
Physical state at 15°C, 1 atm*	Solid	Solid	Liquid	Liquid
Freezing point*	42.35°C (Kirk-Othmer 1982)	21.1°C	4.6°C (Erco PD)	-17.5°C
Boiling point	261°C (Kirk-Othmer 1982)	158°C (Kirk-Othmer 1982)	≈147°C (Kirk-Othmer 1982)	135°C (Kirk-Othmer 1982)
Vapour pressure	0.004 kPa (20°C) (Kirk-Othmer 1982)	0.29 kPa (20°C) (Kirk-Othmer 1982)	-	0.75 kPa (20°C) (Kirk-Othmer 1982)
Densities				
Density (25°C)	1.864 g/mL (Kirk-Othmer 1982)	1.685 g/mL (Kirk-Othmer 1982)	-	1.573 g/mL (Kirk-Othmer 1982)
Specific gravity (25°/4°C)	1.850 (CRC 1980)	1.685	1.628 (Erco PD)	1.574
Vapour density			3.4 (Ashland MSDS 1980)	
Fire Properties				
Flammability	Not combustible (NFPA 1978)			
Decomposition temperature	213°C (initiation of conversion to pyrophosphoric acid) (CRC 1980; Kirk-Othmer 1982)			
Decomposition products	Pyrophosphoric acid → (CCD 1977; CCPA 1983)	Metaphosphoric acid →	Phosphorus oxides (PO_x)	

* Phosphoric acid and solutions are readily supercooled, that is they do not necessarily crystallize at their normal freezing point and may remain liquid at 10 to 20°C below their freezing point for some time.

	100%	85%	80%	75%
Behaviour in a fire	Contact with some metals produces hydrogen which may form flammable mixtures with air (NFPA 1978)			
Other Properties				
Molecular weight of pure substance	98.00 (CRC 1980)	-	-	-
P_2O_5 equivalence (percent)	72.43 (Kirk-Othmer 1982)	61.47 (Kirk-Othmer 1982)	58.0 (Kirk-Othmer 1982)	54.32 (Kirk-Othmer 1982)
Viscosity	140 mPa·s (20°C) (Kirk-Othmer 1982)	28 mPa·s (20°C) (Kirk-Othmer 1982)	-	15 mPa·s (20°C) (Kirk-Othmer 1982)
Hygroscopicity	Hygroscopic (NFPA 1978)			
Latent heat of fusion	10.5 kJ/ mole (at melting point) (CRC 1980)	-	-	-
Heat of formation	-1261.5 kJ/ mole (25°C) (JANAF 1971)	-	-	-
Heat of solution	-11.8 kJ/ mole (CHRIS 1974)	-	-	-
Heat capacity constant pressure (C_p)	106.2 J/ (mole ·°C) (25°C) (JANAF 1971) ≃1.7 J/ (g·°C) (15°C) (Ullmann 1975)	≃1.9 J/ (g·°C) (15°C)	≃2.0 J/ (g·°C) (15°C)	≃2.2 J/ (g·°C) (15°C)
pH of aqueous solution	1.5 (1.0 percent H_3PO_4 solution at 20°C) (Erco PD)			
Electrical conductivity	-	0.078 ohm^{-1} (US DHEW 1970)	-	0.129 ohm^{-1} (US DHEW 1970)
Solubility				
In water	Miscible (Erco PD)			

In other common materials	Soluble in ethanol (CRC 1980)
	Soluble in dioxane (Linke 1958)

Chemical Properties (Kirk-Othmer 1982; Bailar 1973).

Phosphoric acid is a high-volume inorganic acid. In most countries, including Canada, it is second in terms of organic compounds only to sulphuric acid. Phosphoric acid is a tribasic acid; it dissociates in water according to the following scheme (dissociation constants are indicated):

$$H_3PO_4 \underset{K_1=7.1 \times 10^{-3}}{\rightleftharpoons} H_2PO_4^- \underset{K_2=6.3 \times 10^{-8}}{\rightleftharpoons} HPO_4^{2-} \underset{K_3=4.4 \times 10^{-13}}{\rightleftharpoons} PO_4^{3-}$$

In aqueous solutions, all the above species are present in the amounts corresponding to the dissociation constants.

Aside from its acidic behaviour, phosphoric acid is relatively unreactive at room temperature and does not show the strong oxidizing behaviour of many other acids. The reduction of phosphoric acid does not occur to any significant degree below 350 to 400°C. At these temperatures or above, the acid reacts with most metals and their oxides. Phosphoric acid is rated as weaker than sulphuric, nitric, hydrochloric and chromic acids, but stronger than acetic, oxalic, silicic and boric acids.

Pure, 100 percent, phosphoric acid, which is not a commercial product, is a white crystalline (monoclinic) solid that melts at 42.35°C. When the anhydrous product is melted, reorganization takes place in the liquid phase as follows:

$$2\,H_3PO_4 \rightleftharpoons \underset{\text{pyrophosphoric acid}}{H_4P_2O_7} + H_2O$$

If maintained in a molten state for some time, the freezing point falls to an equilibrium value of 34.6°C at a 6 mole percent pyrophosphoric acid content.

The sample history thus affects the melting point; this accounts for the variation in literature values of melting and freezing points. Pure phosphoric acid (and some solutions as well) supercools readily and can be kept for long periods of time at temperatures 10-20°C below the melting point in a liquid state. Three crystal forms have been found; however, that designated 'H_3PO_4-I' is most stable and readily formed.

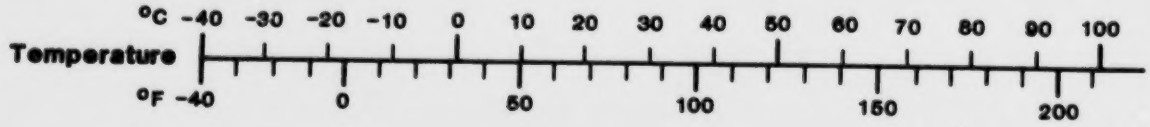
Excess P_2O_5 can be added to aqueous forms; solutions of over 100 percent (equivalent to 100 percent H_3PO_4) can thus be made. They are often called superphosphoric acids. Strong acids (over about 90 percent acid or 67 percent P_2O_5) contain polyphosphoric acids. Only the dimer or pyrophosphoric acid is well characterized and available in crystalline form. The following table shows the equilibrium composition of strong acids:

Acid	Concentration	Percentage Composition				
% P_2O_5	% H_3PO_4	1 (phosphoric acid)	2 (pyrophosphoric acid)	3	4	5
67	94	100	0	0	0	0
69	95	99.7	0.33	0	0	0
74	102	77.1	22.1	0.8	0	0
78	108	33.5	50.6	11.5	2.7	0.7
81	112	12.2	34.0	22.7	14.6	8.4
84	115	3.9	11.8	12.7	12.0	10.5

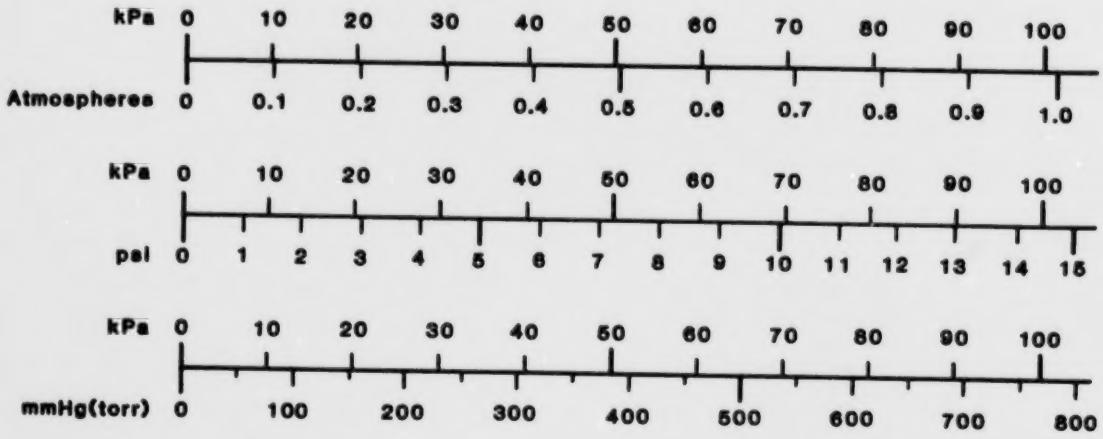
TABLE 1

PHOSPHORIC ACID

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa



Viscosity

Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J

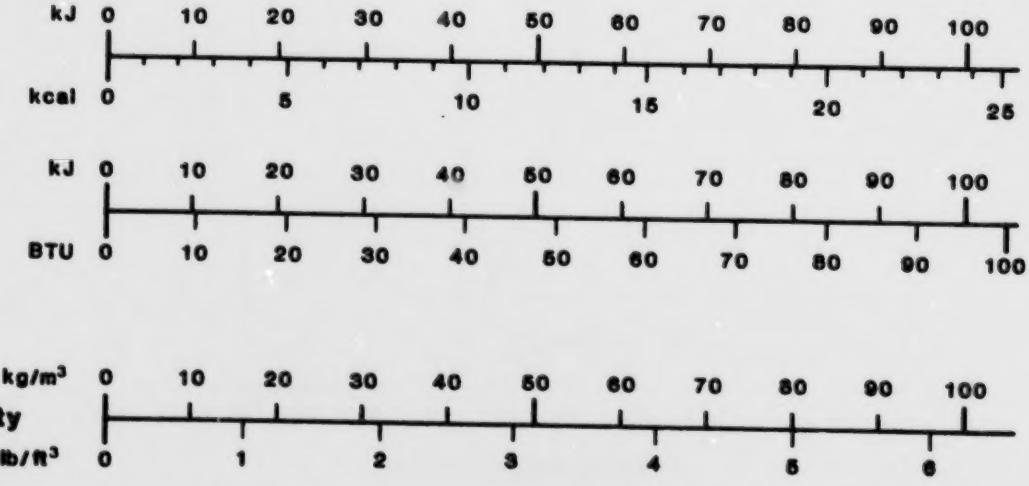


FIGURE 1

PHOSPHORIC ACID

PHASE DIAGRAM OF THE H_2O•H_3PO_4 SYSTEM

Reference: KIRK-OTHMER 1982

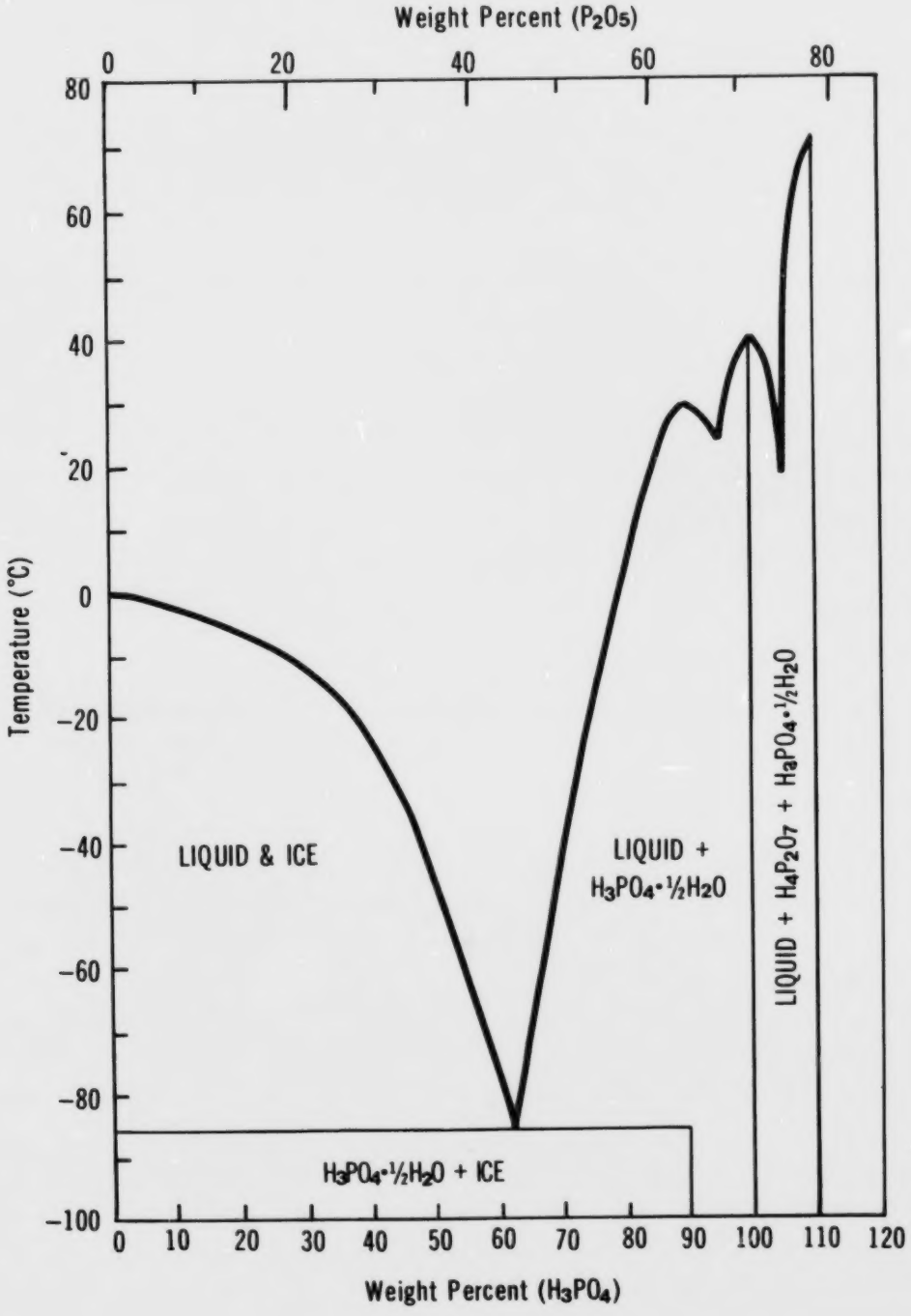


FIGURE 2

PHOSPHORIC ACID

DENSITY OF SOLUTIONS

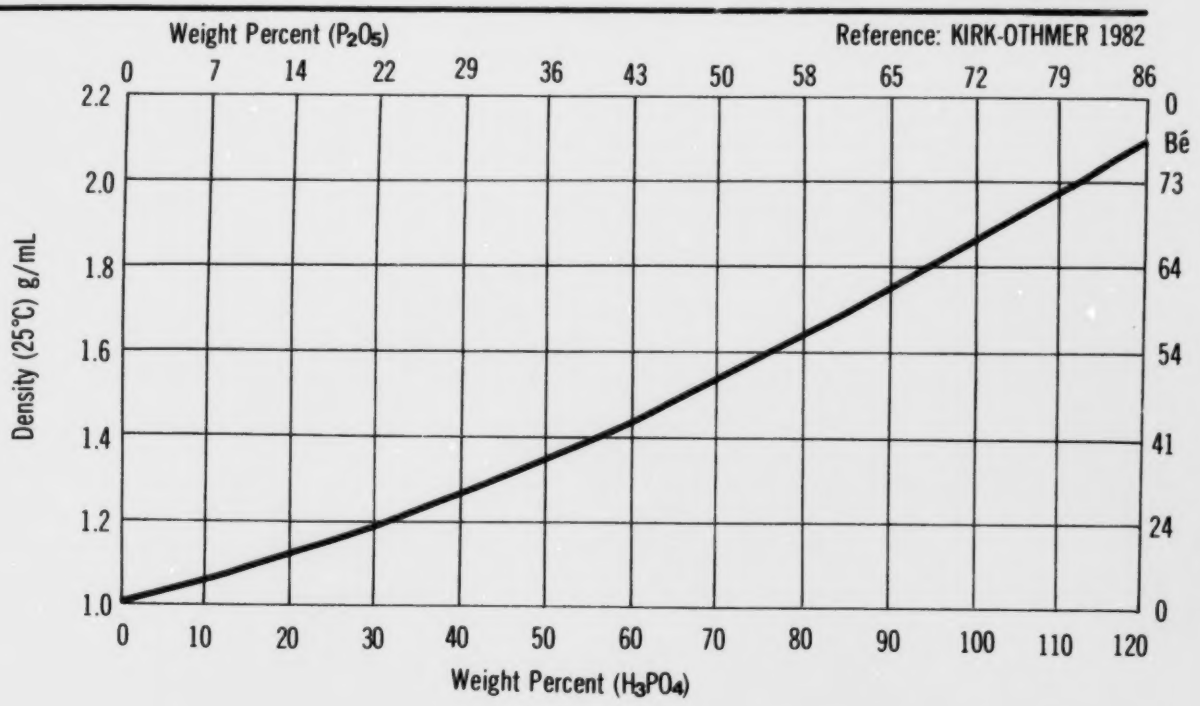


FIGURE 3

PHOSPHORIC ACID

BOILING POINTS OF SOLUTIONS

Reference: KIRK-OTHMER 1982

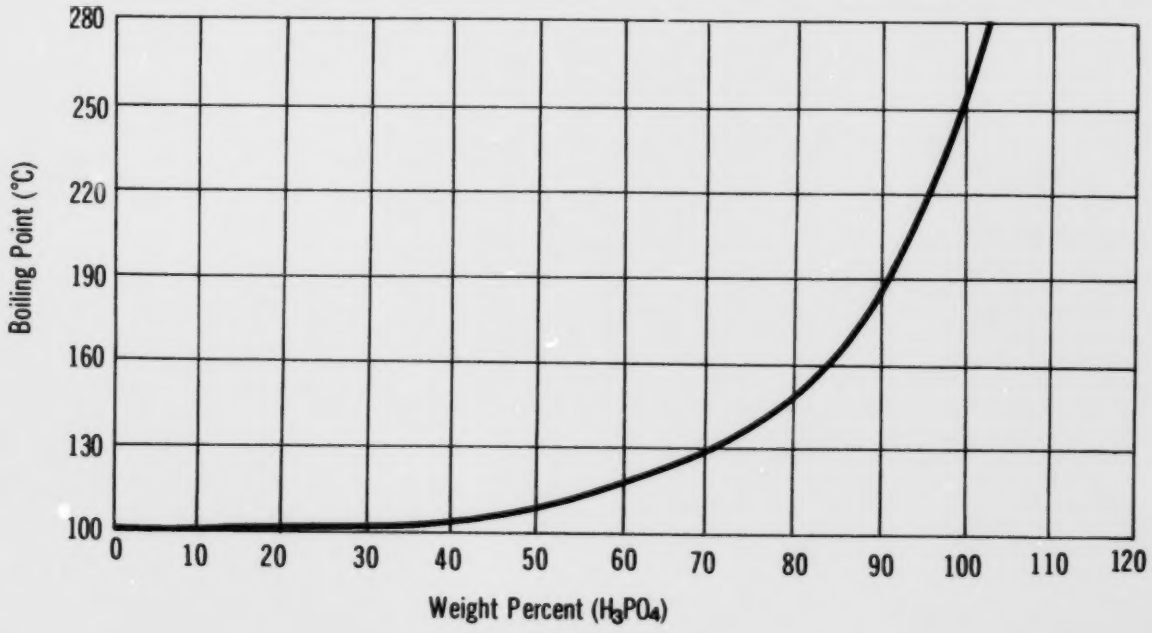


FIGURE 4

PHOSPHORIC ACID

VAPOUR PRESSURE OF SOLUTIONS

Reference: KIRK-OTHMER 1982

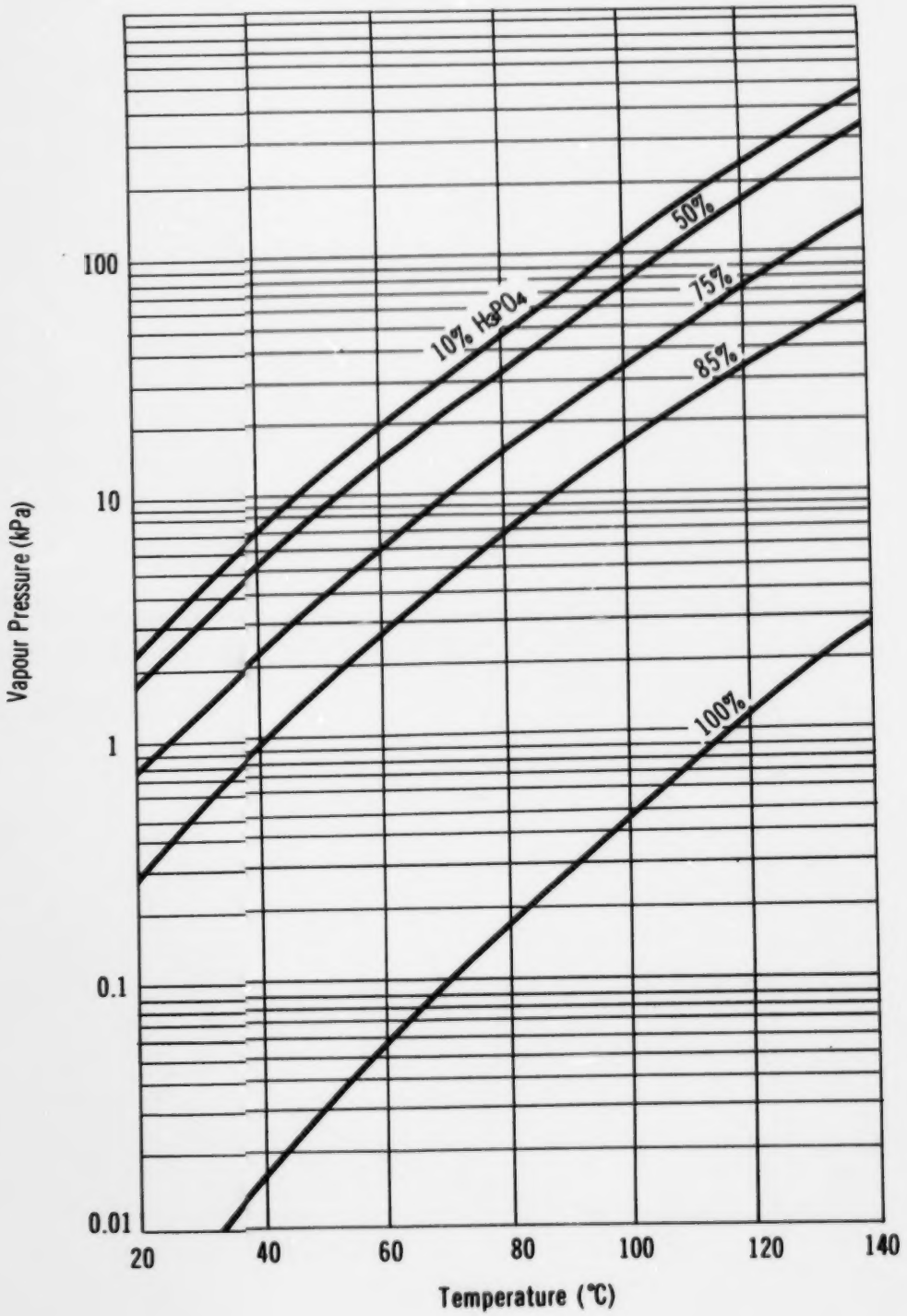


FIGURE 5

PHOSPHORIC ACID

VISCOSITY OF SOLUTIONS

Reference: KIRK-OTHMER 1982

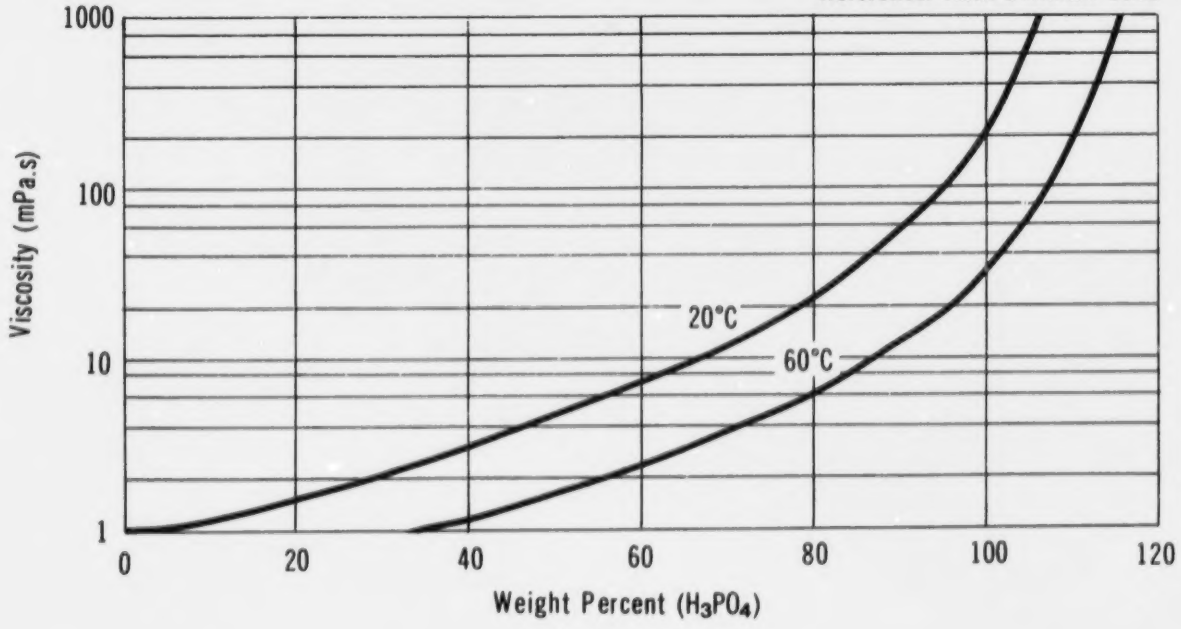
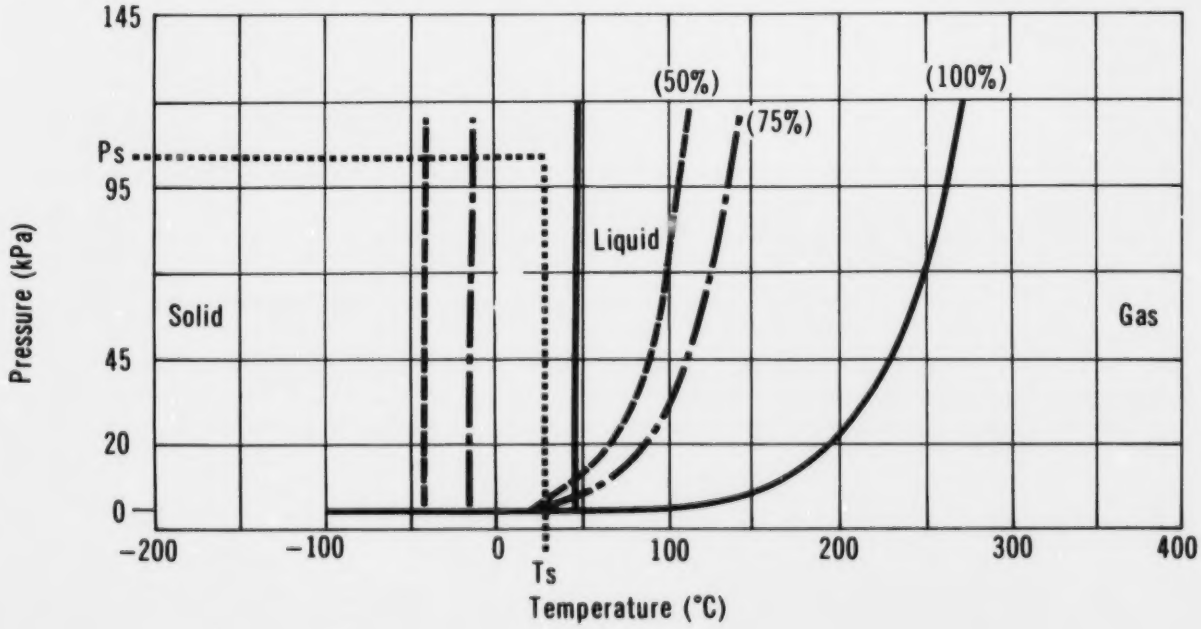


FIGURE 6

PHOSPHORIC ACID

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Corpus 1984; Erco POPA 1981)

Phosphoric acid is sold in concentrations from 33 to 115 percent, with 75, 80 and 85 percent being most common. The grades and concentrations available, the impurities contained therein, and the modes of transportation are tabulated below:

Grade	Concentration (% H_3PO_4)	Concentration (% P_2O_5)	Impurities (mg/L)	Containers
Technical	75	54.4	Arsenic: 40 to 80	Tank Trucks
	80	58.0		Tank Cars
	85	61.6		Cubitainers
	105	76.1		Steel Drums
	115	-		Steel Drums
Food	75	54.4	Chloride: 3,	Tank Trucks
	80	58.0	Arsenic: 3,	Tank Cars
	85	61.6	Heavy Metals: <10 (As, Pb), Iron: 3, Oxidizing Substances: <5	Steel Drums Cubitainers
Pure	85	61.6	Chloride: 2,	Cubitainers
	90	65.3	Arsenic: 0.1, Heavy Metals: <10 (As, Pb), Iron: 3, Oxidizing Substances: <5	
Fertilizer	71.8	52	-	Tank Trucks Tank Cars

3.2 Domestic Manufacturers (Corpus 1984; CBG 1980; Scott 1979; CCPA 1981)

These are corporate headquarters' addresses and are not intended as spill response contacts.

Belledune Fertilizer (Division of
Canada Wire & Cable Ltd.)
147 Laird Drive
Toronto, Ontario
M4G 3W1
(416) 421-0440

C-I-L Inc.
90 Sheppard Avenue East
Willowdale, Ontario
M2N 6H2
(416) 226-6110

Cominco Ltd.
200 Granville Street
Vancouver, British Columbia
V6C 2R2
(604) 282-0611

Erco Industries Ltd.
2 Gibbs Road
Islington, Ontario
M9B 1R1
(416) 239-7111

Esso Chemical Canada
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

International Minerals & Chemical Corp. (Canada) Ltd.
Box 310
Esterhazy, Saskatchewan
S0A 0X0
(306) 745-3931

Sherritt Gordon Mines
Box 28
Commerce Court West
Toronto, Ontario
M5L 1B1
(416) 363-9241

Western Co-operative Fertilizers
11111 Barlow Trail S.E.
P.O. Box 2500
Calgary, Alberta
T2P 2X1
(403) 279-4421

3.3 **Other Suppliers** (Corpus 1984; CBG 1980; Scott 1979)

A & K Petro-Chem Industries Ltd.
710 Arrow Road
Weston, Ontario
M9M 2M1
(416) 746-2991

Allied Chemical Canada
237 Hymus Blvd.
Pointe-Claire, Quebec
H9R 1G3
(514) 697-9210

Anachemia Ltd.
P.O. Box 147
Lachine, Quebec
H8S 4A7
(514) 489-5711

Arliss Chemical Co. Inc.
325 Hymus Blvd.
Pointe-Claire, Quebec
H9R 1G8
(514) 694-2170

Bate Chemical Co. Ltd.
160 Lesmill Road
Don Mills, Ontario
M3B 2T7
(416) 445-7050

Benson Chemicals Ltd.
P.O. Box 10
Freelton, Ontario
L0R 1K0
(416) 659-3351

Canada Colors and Chemicals Ltd.
80 Scarsdale Road
Don Mills, Ontario
M3B 2R7
(416) 924-6831

Canadian Hanson Ltd.
45 Vansco Road
Toronto, Ontario
M8Z 5J7
(416) 255-1371

Canadian Occidental Petroleum
Industrial Chemical Division
100 Amherst Avenue
North Vancouver, British Columbia
V7H 1S4
(604) 929-3441

Cromac Chemical Co. Ltd.
289 Bridgeland Avenue
Toronto, Ontario
M6A 1Z8
(416) 789-7201

Cyanamid Canada Inc.
2255 Sheppard Avenue East
Willowdale, Ontario
M2J 4Y5
(416) 498-9405

Harrisons & Crosfield (Canada) Ltd.
4 Banigan Drive
Toronto, Ontario
M4H 1G1
(416) 425-6500

Kingsley & Keith (Canada) Ltd.
310 Victoria Avenue
Montreal, Quebec
H3Z 2M8
(514) 487-1550

Mallinckrodt Canada Inc.
600 Delmar Avenue
Pointe-Claire, Quebec
H9W 1E6
(514) 695-1220

Monsanto Canada Ltd.
2000 Argentina Road
Plaza 2, 3rd Floor
Mississauga, Ontario
L5M 2G4
(416) 826-9222

Quadra Chemicals Ltd.
7575 TransCanada Highway
St-Laurent, Quebec
H4T 1V6
(514) 337-2454

Recochem Inc.
850 Montée de Liesse
Montreal, Quebec
H4T 1P4
(514) 341-3550

Shefford Chemicals Ltd.
1028 Principale
Granby, Quebec
J2G 8C8
(514) 378-0125

Simplot Chemical Co. Ltd.
P.O. Box 940
Brandon, Manitoba
R7A 6A1
(204) 728-5701

Uba Chemical Industries Ltd.
2605 Royal Windsor Drive
Mississauga, Ontario
L5J 1K9
(416) 823-6460

Van Waters and Rogers Ltd.
9800 Van Horne Way
Richmond, British Columbia
V6X 1W5
(604) 273-1441

3.4 Major Transportation Routes

Current Canadian production of phosphoric acid is located primarily in Alberta, in Redwater, Calgary, Medicine Hat and Fort Saskatchewan. Other production facilities are in Portland, Courtright and Port Maitland, Ontario, and in British Columbia, New Brunswick and Quebec. A large portion of phosphoric acid is used near the production plant to produce fertilizers. A small portion is distributed widely across Canada.

3.5 Production Levels (Corpus 1984)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Belledune, Belledune, N.B.	136
C-I-L, Courtright, Ont.	85
Cominco, Kimberly, B.C.	86
Cominco, Trail, B.C.	76
Erco Industries, Port Maitland, Ont.	70
Erco Industries, Buckingham, Que.	20
Esso Chemical Canada, Redwater, Alta.	290
International Minerals and Chemical Canada, Port Maitland, Ont.	118
Sherritt Gordon Mines, Ft. Saskatchewan, Alta.	60
Western Cooperative Fertilizers, Calgary, Alta.	142
Western Cooperative Fertilizers, Medicine Hat, Alta.	67
TOTAL	1150
Domestic Production (1982)	635
Imports (1982)	14.6
TOTAL SUPPLY	649.6

3.6 Manufacture of Phosphoric Acid

3.6.1 General (Kirk-Othmer 1982; US DHEW 1970; Corpus 1984). Both wet and thermal processes are used in Canada to manufacture phosphoric acid, the former accounting for 94 percent of production in 1983. In the "wet process", phosphoric acid is produced from the reaction of phosphate rock and 93 percent sulphuric acid. In the "thermal" or "furnace" process, elemental white (yellow) phosphorus is oxidized to produce P_2O_5, which is hydrolyzed to the acid.

3.6.2 Manufacturing Process.

3.6.2.1 Wet process. Phosphate rock is ground (generally in a ball mill) to about 200 mesh, mixed with dilute (recycled) phosphoric acid ("pre-mix"), and added to an agitated digester. Sulphuric acid is then added to the digester; it reacts with the rock to form phosphoric acid:

$$CaF_2 \cdot 3Ca_3(PO_4) + 10H_2SO_4 + 20H_2O \rightarrow \underset{\text{(gypsum)}}{10CaSO_4 \cdot 2H_2O} + 2HF + 6H_3PO_4$$

"Pre-mixing" with phosphoric acid is necessary to prevent the formation of insoluble sulphates on the particle surfaces. The reaction mixture must also be maintained at temperatures low enough to form gypsum and not anhydrite ($CaSO_4$) which would subsequently hydrate and plug piping. Some of the silica and fluorine may react to produce Na_2SiF_6 which also precipitates.

The gypsum-acid slurry is then filtered and washed to separate phosphoric acid from gypsum. The acid at this stage is about 30 percent P_2O_5; it may be further concentrated or used as is. Dilute acid from the washings is recycled to the pre-mix step. Off-gas is scrubbed with alkali to remove hydrogen fluoride before venting.

3.6.2.2 Furnace process. White (yellow) phosphorus is burned in air to form the pentoxide. The phosphorus pentoxide is hydrated to the acid. The following reactions apply:

$$P_4 + 5O_2 \rightarrow 2P_2O_5$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

The phosphorus burning is carried out in a wetted-wall reactor where the P_2O_5 formed reacts with the water directly or in an air-cooled combustion chamber, after which the pentoxide is fed to a separate hydrator.

3.7 Major Uses in Canada (Corpus 1984)

Phosphoric acid is used in the production of ammonium phosphate, triple super phosphate, dicalcium phosphate, liquid fertilizer, sodium phosphates, calcium phosphates, various other phosphate salts, in metal finishing, in food and in beverages. In 1982, 80 percent of domestic production was used for ammonium phosphate production, 9 percent for dicalcium phosphate production, 4 percent for sodium phosphate production, and 2 percent was exported.

3.8 Major Buyers in Canada (Corpus 1984)

Admiral Sanitation, Toronto, Ont.
Alpine Fertilizer, Kitchener, Ont.
Amchem Products, Windsor, Ont.
Armalite, Toronto, Ont.
Coca-Cola, Toronto, Ont.
Cyanamid Canada, Niagara Falls, Ont.
Diversey Wyandotte, Mississauga, Ont.
DuBois Chemicals, Toronto, Ont.
Economics Laboratory, Toronto, Ont.
Kert Chemical, Toronto, Ont.

Na-Churs Plant Food, London, Ont.
Oakite Products, Bramalea, Ont.
Pennwalt of Canada, Oakville, Ont.
Pepsi-Cola Canada, Toronto, Ont.
Simplot Chemical, Brandon, Man.
Van Camp Products, Toronto, Ont.
WW Wells, Toronto, Ont.
West Chemical, Montreal, Que.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Phosphoric acid solutions are shipped bulk in railway tank cars and tank motor vehicles. The most common strengths transported are 75, 80 and 85 percent.

4.1.1.1 Railway tank cars. Railway tank cars used in the transportation of phosphoric acid are listed in Table 2 (RTDCR 1974; TCM 1979). Railway tank cars are either of stainless steel or lined carbon steel. Figure 7 shows a 111A100W1 railway car used to transport phosphoric acid. Table 3 indicates railway tank car details associated with this drawing. Phosphoric acid cars are never unloaded through bottom outlets; the cars are unloaded from the top using a pump or compressed air (MCA 1958). The acid is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with a 51 mm (2 in.) unloading connection valve. Air pressure at 207 kPa (30 psi) maximum is applied through the 25 mm (1 in.) air connection valve. Outside heating coils and fibreglass insulation are required for certain strengths of acid that freeze at common winter temperatures (MCA 1958).

4.1.1.2 Tank motor vehicles. Similar to railway tank cars, highway tankers are unloaded from the top, usually with the stand pipe being extended down over the back of the tank. Compressed air may be used for unloading; however, unloading by pump is preferred (MCA 1958). The air inlet is usually a 25 mm (1 in.) diameter male threaded connection located at the top of the trailer through which air pressure not exceeding 207 kPa (30 psi) may be applied. Tanks may be insulated and heated depending on acid strength freezing point.

Tank motor vehicles should conform to Transport Canada Specification TC312, covering MC310, MC311 and MC312, as outlined in Table 4 (TDGC 1980). Specifications MC303, MC304, MC306 and MC307 are also permitted (CCPA 1983). Phosphoric acid solutions are not transported under pressure. Highway tankers must be pressure tested at 311 kPa (45 psi) minimum to allow for the compressed air pressure of 207 kPa (30 psi) used during top unloading (MCA 1958). The maximum working pressure of the tanker is in effect 207 kPa (30 psi).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
103BW	Steel fusion-welded tank with dome. Uninsulated or insulated. Rubber-lined tank. 1% dome. Safety vent (414 kPa) (60 psi). Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 414 kPa (60 psi).
103EW	Alloy (stainless) steel fusion-welded tank with dome. Insulated or uninsulated. 1% dome. Bottom outlet prohibited, bottom washout optional. Top unloading arrangement required. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi).
111A60W2	Steel fusion-welded tank without dome. Uninsulated or insulated. Interior lined. 2% minimum outage. Gauging device. Top unloading arrangement required. Bottom outlet prohibited; bottom washout optional. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Test pressure 414 kPa (60 psi).
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Rubber-lined for phosphoric acid. Gauging device. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Bottom outlet prohibited, bottom washout optional. Test pressure 414 kPa (60 psi).
111A60W5	Steel fusion-welded tank without dome. Uninsulated or insulated. Rubber-lined tank. 2% minimum outage. Gauging device. Safety vent (414 kPa) (60 psi). Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 414 kPa (60 psi).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (Cont'd)

CTC/DOT* Specification Number	Description
111A100W1	Steel fusion-welded tank without dome. Rubber-lined for phosphoric acid service. Uninsulated or insulated. 2% minimum outage. Safety valve. Bottom outlet or washout optional but not used for phosphoric acid service. Safety valve 517 kPa (75 psi) or safety vent 690 kPa (100 psi). Test pressure 690 kPa (100 psi).

* Canadian Transport Commission and Department of Transportation (U.S.)

4.1.2 Packaging. In addition to bulk shipments, phosphoric acid is also transported in smaller containers. A variety of construction materials are permitted, as listed in Table 5 (RTDCR 1974).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1958):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed.
- A safe operating platform must be provided at the unloading point.
- Effectively ground the tank car.

Proceed with off-loading as follows (MCA 1958):

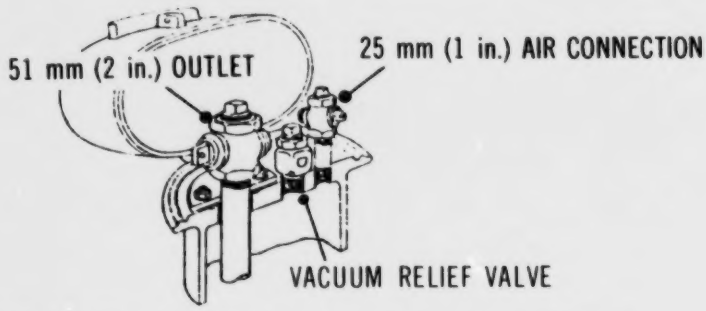
- In cold weather, for certain strengths of acid (80 and 85 percent strengths), connect the heating coil connection valves to the hot water line. Vents on the tank car must be opened before any heat is applied.

FIGURE 7

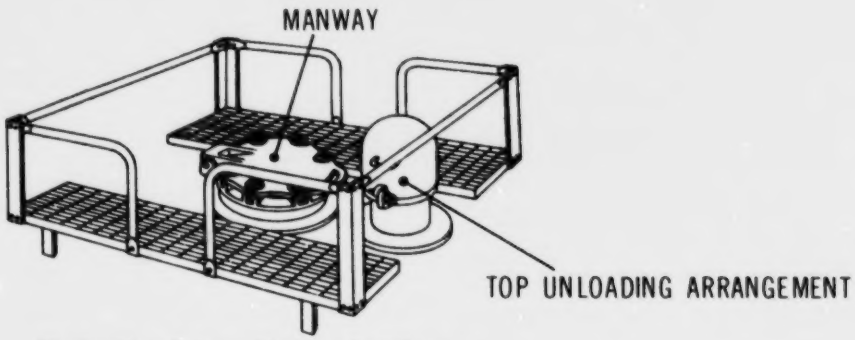
PHOSPHORIC ACID

RAILWAY TANK CAR - CLASS 111A100W1

(Reference - TCM 1979; RTDCR 1979)



Detail of top unloading arrangement



Detail of loading platform

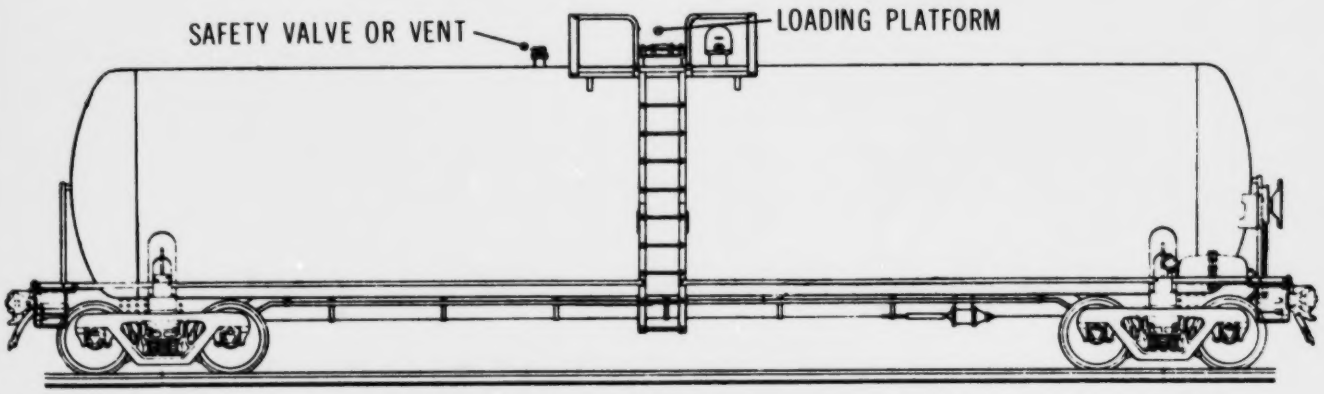


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A100W1 (TCM 1979; RTDCR 1974)

Description	Tank Car Size (Imp. Gal.) 14 000	16 700	25 000
Overall			
Nominal capacity	64 400 L (14 000 gal.)	75 700 L (16 700 gal.)	114 000 L (25 000 gal.)
Car weight - empty	28 600 kg (63 000 lb.)	39 500 kg (65 000 lb.)	31 800 kg (70 000 lb.)
Car weight - max.	119 000 kg (263 000 lb.)	119 000 kg (263 000 lb.)	119 000 kg (263 000 lb.)
Tank			
Material	Steel	Steel	Steel
Thickness	11.1 mm (7/16 in.)	11.1 mm (7/16 in.)	11.1 mm (7/16 in.)
Liner	4.8 mm (3/16 in.) rubber	4.8 mm (3/16 in.) rubber	4.8 mm (3/16 in.) rubber
Inside diameter	2.60 m (102 in.)	2.74 m (108 in.)	2.84 m (112 in.)
Test pressure	689 kPa (100 psi)	689 kPa (100 psi)	689 kPa (100 psi)
Burst pressure	3450 kPa (500 psi)	3450 kPa (500 psi)	3450 kPa (500 psi)
Approximate Dimensions			
Coupled length	14 m (46 ft.)	16 m (51 ft.)	20 m (66 ft.)
Length over strikers	13 m (43 ft.)	15 m (48 ft.)	19 m (63 ft.)
Length of truck centres	10 m (32 ft.)	12 m (38 ft.)	16 m (52 ft.)
Height to top of grating	4 m (12 ft.)	4 m (12 ft.)	4 m (12 ft.)
Overall height	4 m (14 ft.)	4 m (15 ft.)	4 m (15 ft.)
Overall width (over grabs)	3.2 m (127 in.)	3.2 m (127 in.)	3.2 m (127 in.)
Length of grating	2.4 m (8 ft.)	2.4 m (8 ft.)	2.4 m (8 ft.)
Width of grating	1.8 m (6 ft.)	1.8 m (6 ft.)	1.8 m (6 ft.)
Loading/Unloading Fixtures			
Top Unloading			
Unloading connection	51 mm (2 in.)	51 mm (2 in.)	51 mm (2 in.)
Manway/fill hole	203-356 mm (8-14 in.)	203-356 mm (8-14 in.)	203-356 mm (8-14 in.)
Air connection	25-51 mm (1-2 in.)	25-51 mm (1-2 in.)	25-51 mm (1-2 in.)
Bottom Unloading			
Bottom outlet	Not used	Not used	Not used
Safety Devices	Safety vent or valve; vent set at 690 kPa (100 psi), valve set at 517 kPa (75 psi)		
Dome	None		
Insulation	Optional		

TABLE 4 TANK MOTOR VEHICLE SPECIFICATIONS

TC* Specification Number	Description
TC312	Steel butt-welded tank. Design and construct in accordance with ASME Code when unloading by pressure in excess of 103 kPa (15 psi). Gauging device not required. Top and/or bottom discharge outlet. Minimum one pressure relief device per compartment as required by ASME Code. One minimum 380 mm (15 in.) diameter manhole per compartment. Bottom washout optional.

* Transport Canada

TABLE 5 CONTAINERS FOR PHOSPHORIC ACID SERVICE

CTC/DOT Specification Number(s)	Type and Description
1A, 1B, 1C, 1D	Glass carboys in boxes, kegs or plywood drums
15A, 15B, 15C, 16A, 19A	Glass or polyethylene containers in wooden boxes
5D	Rubber-lined metal drums
12A, 12B	Polyethylene containers in fibreboard boxes
22C with 2T polyethylene containers	Polyethylene containers in plywood or wooden boxes
37p	Polyethylene liners in a steel drum

- Connect the 51 mm (2 in.) unloading line to the discharge outlet and connect the 25 mm (1 in.) air line. Air pressure must be reduced to 207 kPa (30 psi) for unloading. A safety relief valve must be installed in the air line to release at 242 kPa (35 psi).
- After opening the air supply valve, the unloading connection valve can then be opened to unload the car.

- Once the car is empty, the air supply valve must be closed and the vent valve in the air line opened to allow the line pressure to equalize to atmospheric pressure.
- Reverse the above procedure to close up the car.

4.2.2 Off-loading Equipment and Procedures for Tank Motor Vehicles. The unloading of phosphoric acid tank trailers is similar to that of railway tank cars.

4.2.3 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in phosphoric acid service. It is recognized that other materials may be used for particular applications, as indicated in Table 6. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets, pumps and storage tanks.

Schedule 40 seamless ASTM A106 carbon steel, rubber-lined, or Schedule 40 stainless steel 316 pipes are recommended (MCA 1958). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak. The pipeline should be tested with air at pressures from 345 to 518 kPa (50-75 psi) and all leaks carefully stopped. The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on acid tank cars; however, process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining and may be insulated, depending upon acid strength. These lines can be electrically traced or steam-traced with 9 or 13 mm (3/8 or 1/2 in.) copper tubing or steel pipe located inside the insulation, or hot water jacketed (MCA 1958; CCPA 1983).

Stainless steel pipes and swivel joints may be used for flexible sections when handling phosphoric acid. Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance. Flexible acid hose may also be used.

Quick acting ball or plug valves in "20" alloy will serve adequately in all phosphoric acid applications (JSSV 1979).

Neoprene rubber can be used as a gasket material in all phosphoric acid strengths at normal temperatures (GPP).

A single-suction centrifugal pump with "20" alloy shaft and impeller and a high silicon cast iron casing is recommended for pumping.

Welded steel tanks with rubber lining or stainless steel storage tanks are commonly used. Fibre-reinforced plastic or PVC-lined steel may be used for solutions up to 85 percent phosphoric acid (MCA 1958).

The Tennessee Valley Authority has documented its experience with storage tanks (Barber 1974). Storage tanks up to 12 000 000 L (2 600 000 gal.) exist; however, they generally fall in the range of 75 000 L (16 700 gal.) to 4 000 000 L (830 000 gal.). Type 316 stainless steel has been found to be the best material; however, some tanks have used 10 mm (3/8 in.) steel plate with a SS 316 - 14 gauge liner. The corrosion rate of SS 316 at 65°C is almost nil but at 93°C is a few hundredths of a millimetre per year. The stainless steel liners are not recommended except as an improvisation to correct leakage in older carbon steel tanks. Rubber-lined tanks with liners 6 or 4 mm (1/4 or 3/16 in.) thick serve well for lower concentrations only.

4.3 Compatibility with Materials of Construction

The compatibility of phosphoric acid with materials of construction is indicated in Table 6. The unbracketed abbreviations are described in Table 7. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings*	10%	79	PVDC (DCRG 1978)		
		107	PVDF PP (DCRG 1978)		
		121	Chlorinated Polyether (DCRG 1978)		
	25%	79	PVDC (DCRG 1978)		
		107	PP (DCRG 1978)		
		121	Chlorinated Polyether (DCRG 1978)		

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings* (Cont'd)	25%	135	PVDF (DCRG 1978)		
	0-25%	23	PVC I PVC II (DPPED 1967)	PE (DPPED 1967)	
		49		PE (DPPED 1967)	
		60		PVC I PVC II (DPPED 1967)	
	25-50%	23	PVC I PVC II (DPPED 1967)		
		60		PVC I PVC II (DPPED 1967)	
	50-85%	23	PE, ABS PVC I PVC II (DPPED 1967)		
		49	PE (DPPED 1967)		
		60	PVC I (DPPED 1967)	PVC II (DPPED 1967)	
		71			ABS (DPPED 1967)
	75%	52	PVDC (DCRG 1978)		
		107	PVDF PP (DCRG 1978)		
		121	Chlorinated Polyether (DCRG 1978)		
	<85%	To operating limit of material	PVC I** PE** (MWPP 1978)		

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings* (Cont'd)	<85%	24	ABS (MWPP 1978) CS Rubber-lined FRP (Sherritt MSDS 1976)		
	All	To boiling	SS 316 (CCPA 1983)		
2. Valves	All, Chemically Pure	21	"20" Alloy SS 316 (JSSV 1979)		
3. Pumps	100%	82	GRP with FPM A "O" Ring		
4. Storage	100%	<65°C	SS 316, NR, BR Liners (Barber 1974)		
	>100%	>65°C	SS316 (Barber 1974)		NR (as Liner) (Barber 1974)
5. Others	10%	20	SS 302 SS 304 SS 316 (ASS)		SS 410 SS 430 (ASS)
		60	PVC (TPS 1978)		
		82	PP (TPS 1978)		
		85	CPVC (TPS 1978)		
	25, 50%	60	PVC (TPS 1978)		
		66	PVDF (TPS 1978)		
		82	PP (TPS 1978)		
		85	CPVC (TPS 1978)		
	Up to 30%	60	PE, PP NR, NBR IIR, EPDM CR, FPM CSM (GF)	uPVC (GF)	POM (GF)

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)	50%		NR, SBR CR, NBR IIR, CSM EPDM (GPP)		
	50, 85%	60	PVC (TPS 1978)		
		66	PVDF (TPS 1978)		
		82	PP (TPS 1978)		
		100	CPVC (TPS 1978)		
	80%	60	SS 302 SS 304 SS 316 (ASS) uPVC, PP NR, IIR EPDM, CR FPM CSM (GF)	PE (GF)	POM NBR (GF)
		100	CSM (GF)	IIR EPDM FPM (GF)	uPVC, PE PP, POM NR, NBR CR (GF)
	85%		NR, SBR CR, NBR IIR, CSM EPDM (GPP)		
	90%	100	CSM (GF)	IIR EPDM FPM (GF)	uPVC, PE PP, POM NR, NBR CR (GF)
	Satu-rated	20	SS 302 SS 304 SS 316 (ASS)		SS 430 (ASS)

*Note: The plastics documented here are suitable for liners or temporary service and not for long-term service as stand alone pipes.

** This material has been given a lower rating in a similar application by another reference.

TABLE 7 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
BR	Butyl Rubber
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
FRP	Fibre Reinforced Plastic
	Glass
GRP	Glass Reinforced Vinyl Ester
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel
	Nickel-Copper Alloy (Monel)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride (Saran)
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
SS (Followed by grade)	Stainless Steel
	"20" Alloy (Durimet 20, Carpenter 20)
uPVC	Unplasticized Polyvinyl Chloride

5 CONTAMINANT TRANSPORT

5.1 General Summary

Phosphoric acid is normally transported as an aqueous solution of 75 to 85 percent concentration in railway tank cars and tank trucks. Phosphoric acid is miscible with water. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may cause environmental problems.

Because phosphoric acid is essentially nonvolatile, dispersion in air is not a problem. The following factors are considered for the transport of a spill in water and soil:

Contaminant Transport	Leak from tank	Rate of discharge Percent remaining
	Water	Diffusion and downstream concentration
	Soil	Depth and time of penetration

It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Phosphoric acid solution is commonly transported in railway tank cars and tank trucks as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with phosphoric acid is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple

means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the relatively low volatility of phosphoric acid and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

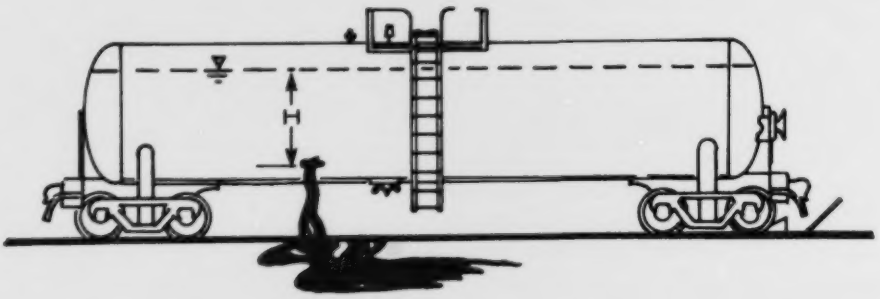


FIGURE 8 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

The rate of outflow (q) from a vent hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). It is a function of the hole size (A) and shape, the height of the liquid above the puncture hole (H) and a coefficient of discharge (Cd). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed. The viscosities of phosphoric acid solutions vary widely and thus only the 80 percent solution was chosen for the nomograms. The discharge rate varies directly as the square root of the density; this may be used to estimate discharges of other solutions.

5.2.2 Nomograms.

5.2.2.1 Figure 9: Percent remaining versus time. Figure 9 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of phosphoric acid. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

FIGURE 9

PHOSPHORIC ACID (80%)

PERCENT REMAINING VS TIME

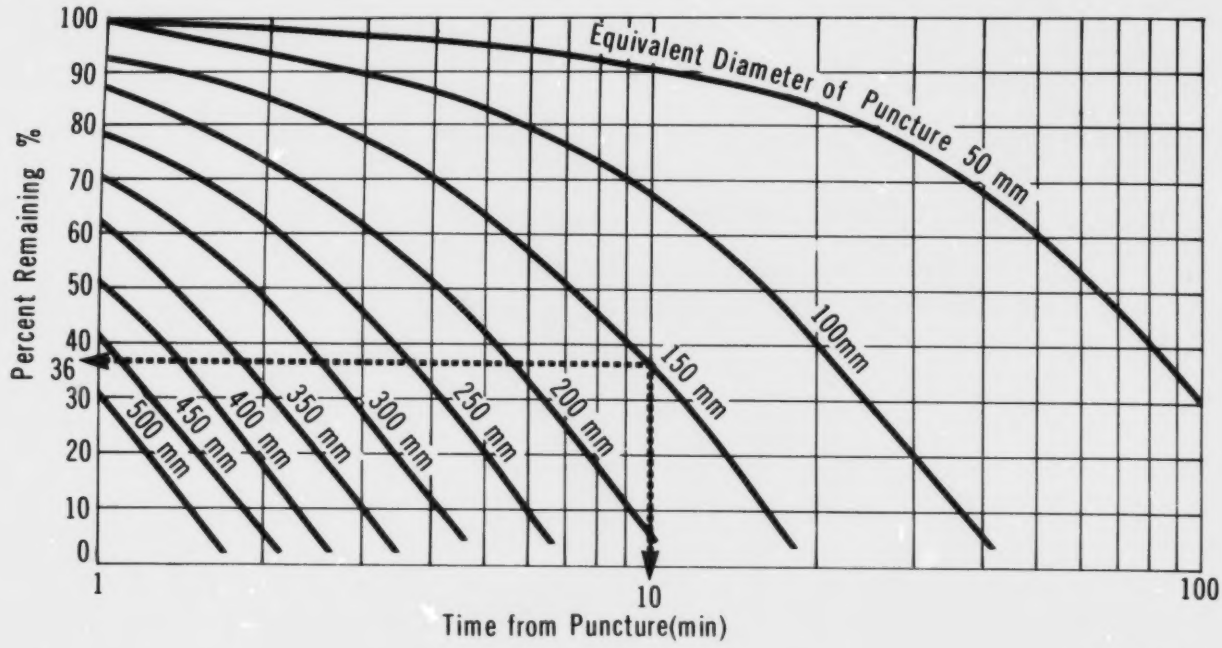
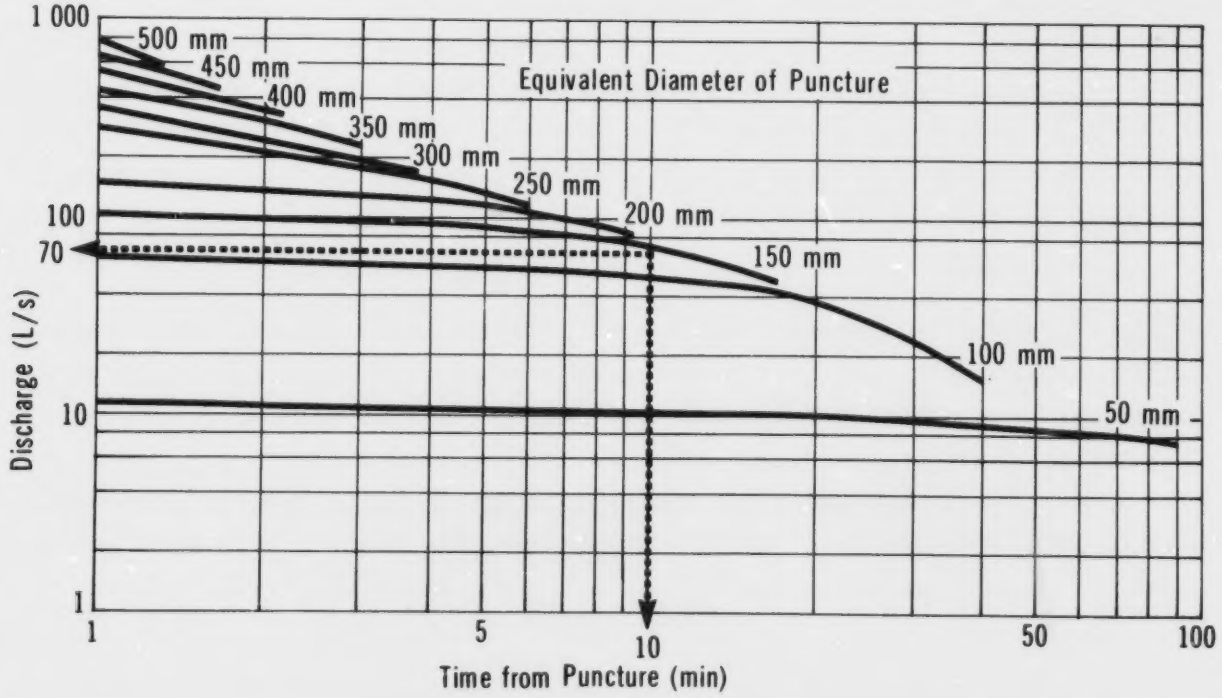


FIGURE 10

PHOSPHORIC ACID (80%)

DISCHARGE RATE VS TIME



5.2.2.2 Figure 10: Discharge rate versus time. Figure 10 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with phosphoric acid has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 9
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- Use Figure 10
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

Because phosphoric acid is nonvolatile in foreseeable spill circumstances, there is no significant potential for dispersion in the air.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, phosphoric acid will mix and dissolve rapidly. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream

of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 (W/d <100) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.2 Nomograms. The following nomograms are presented to calculate concentrations in non-tidal rivers and in lakes (still water).

Non-tidal Rivers

Figure 12: time versus distance for a range of average stream velocities

Figure 13: hydraulic radius versus channel width for a range of stream depths

Figure 14: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 15: alpha* versus diffusion coefficient for various time intervals

Figure 16: alpha versus delta* for a range of spill sizes

Figure 17: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 18: volume versus radius for the hazard zone for a range of lake depths

Figure 19: average concentration versus volume for the hazard zone for a range of spill sizes

The flowchart in Figure 11 outlines the steps required to estimate downstream concentrations after a spill and identifies the nomograms to be used. These nomograms (Figures 12 through 19) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 12: Time versus distance. Figure 12 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 12.

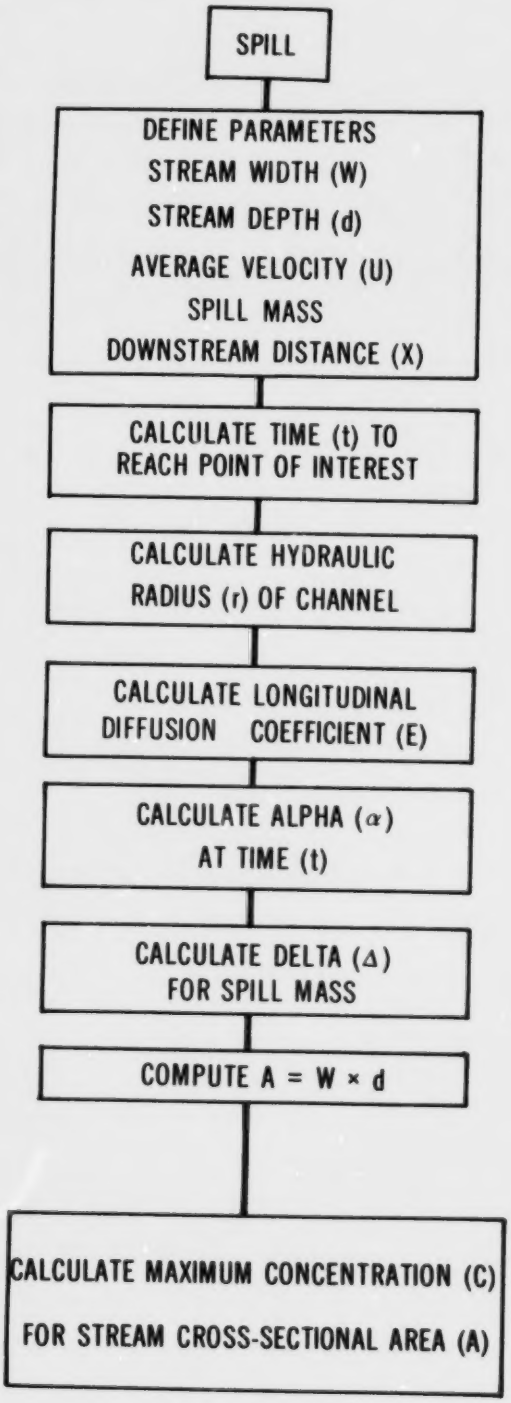
---

* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

FIGURE 11

PHOSPHORIC ACID

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = _____ m

d = _____ m

U = _____ m/s

MASS = _____ tonnes

X = _____ m

Step 2: Use Figure 12

t = _____ minutes

Step 3: Use Figure 13

r = _____ m

Step 4: Use Figure 14

E = _____ m^2/s

Step 5: Use Figure 15

α = _____

Step 6: Use Figure 16

Δ = _____

Step 7: Compute stream cross-sectional Area (A)

A = W × d _____ m^2

Step 8: Use Figure 17

C = _____ ppm

FIGURE 12

PHOSPHORIC ACID

TIME vs DISTANCE

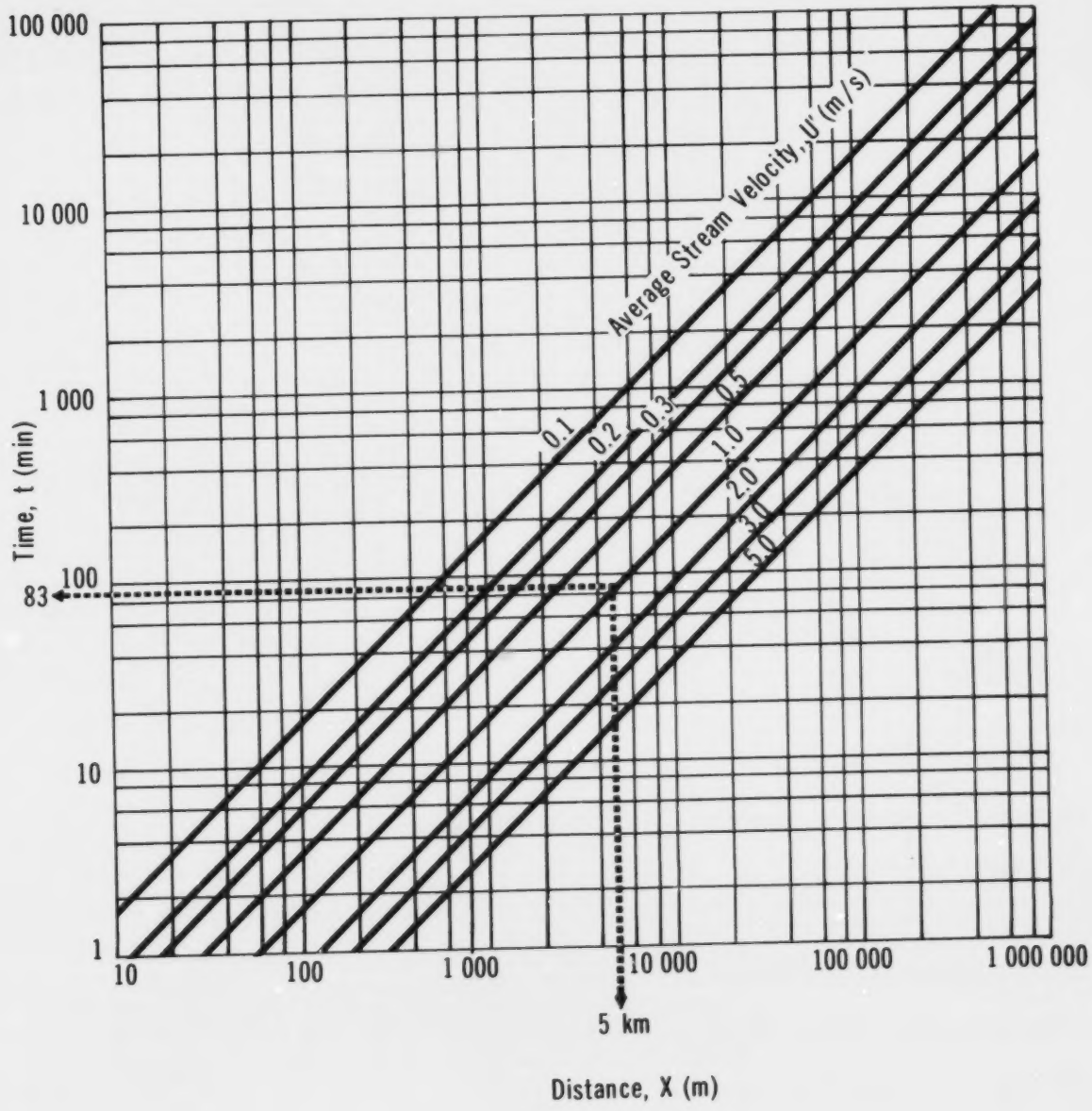


Figure 13: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d).

The hydraulic radius (r) for the channel is required in order to estimate the longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 13 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 14: Diffusion coefficient versus hydraulic radius. Figure 14 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 13 and the average stream velocity (U).

Figure 15: Alpha versus diffusion coefficient. Figure 15 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 16: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 16 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 17: Maximum concentration versus delta. Figure 17 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 17 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 18: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 18. The radius (r) represents the distance from the spill to the point of interest.

Figure 19: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 19 for a known mass of spill. This assumes

FIGURE 13

PHOSPHORIC ACID

HYDRAULIC RADIUS VS CHANNEL WIDTH

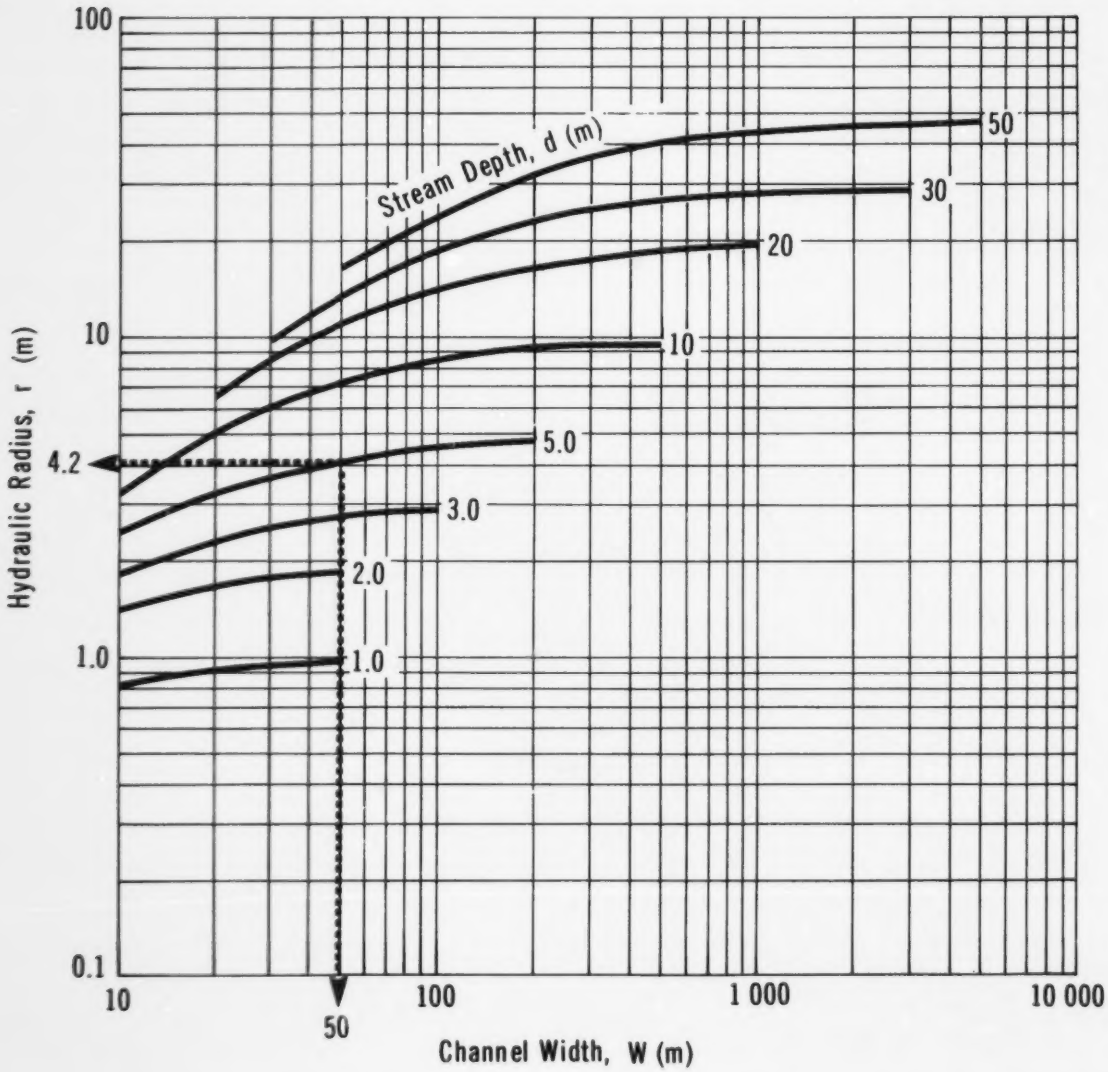


FIGURE 14

PHOSPHORIC ACID

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS

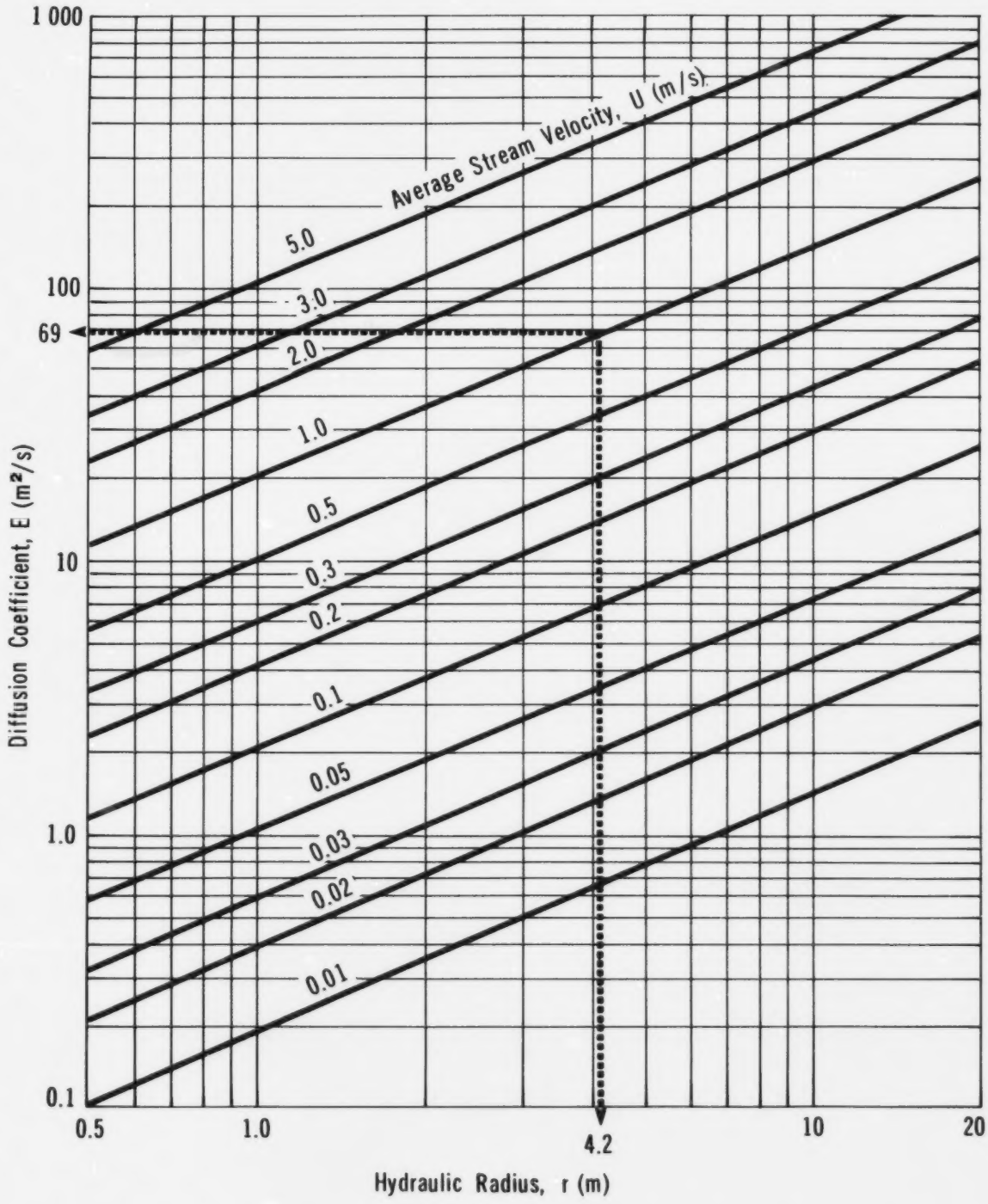


FIGURE 15

PHOSPHORIC ACID

ALPHA vs DIFFUSION COEFFICIENT

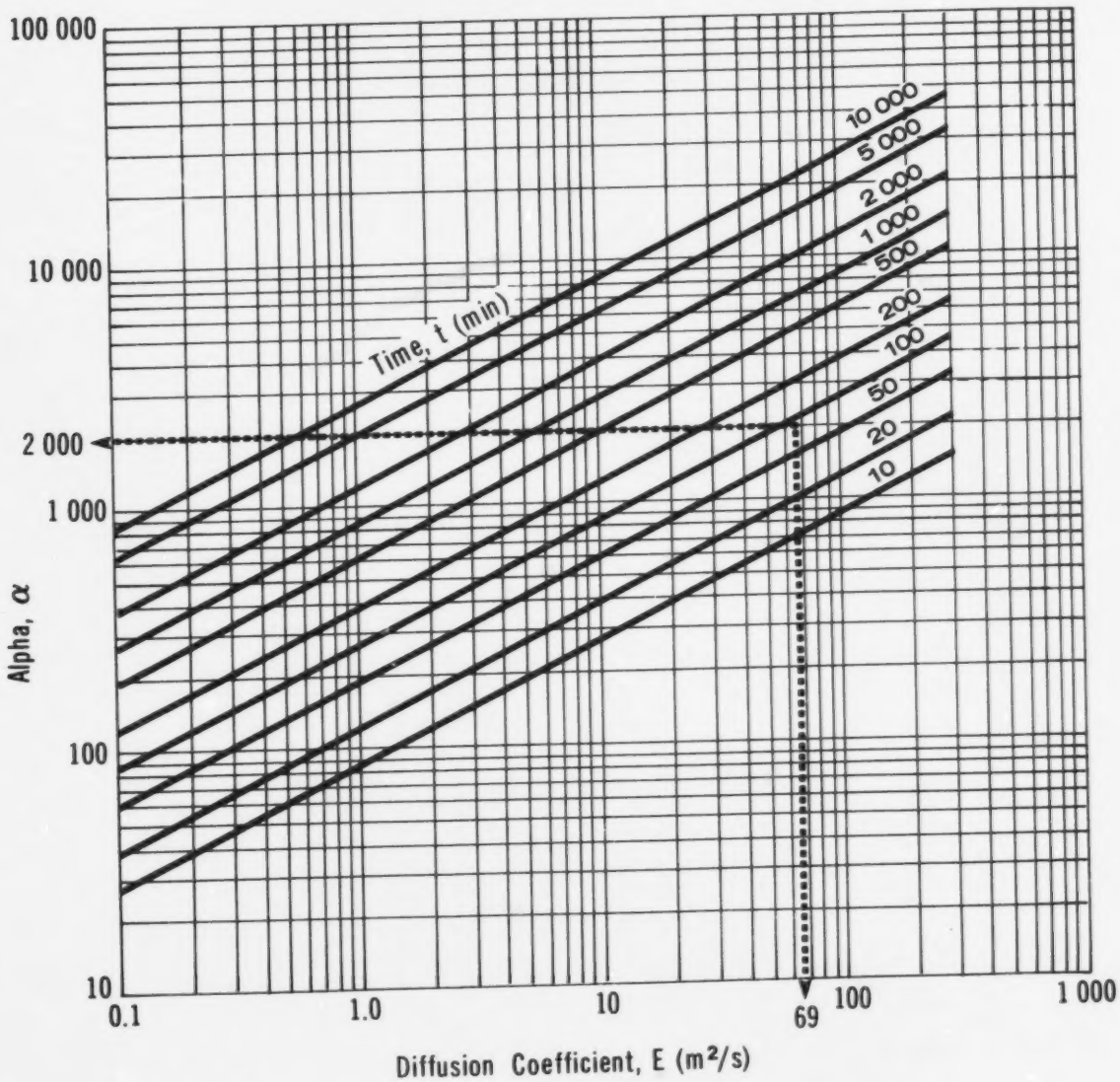


FIGURE 16

PHOSPHORIC ACID

ALPHA vs DELTA

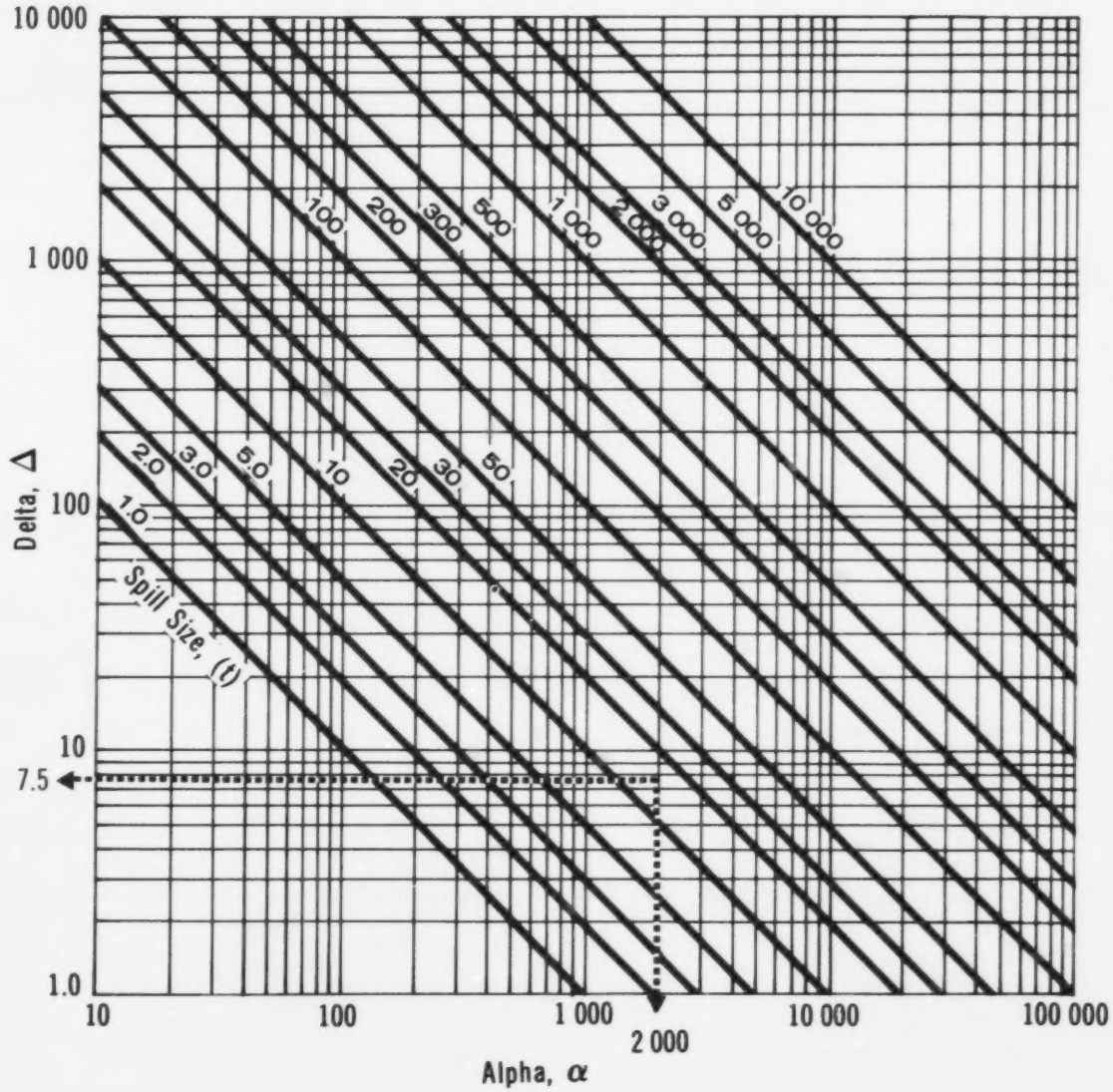


FIGURE 17

PHOSPHORIC ACID

MAXIMUM CONCENTRATION vs DELTA

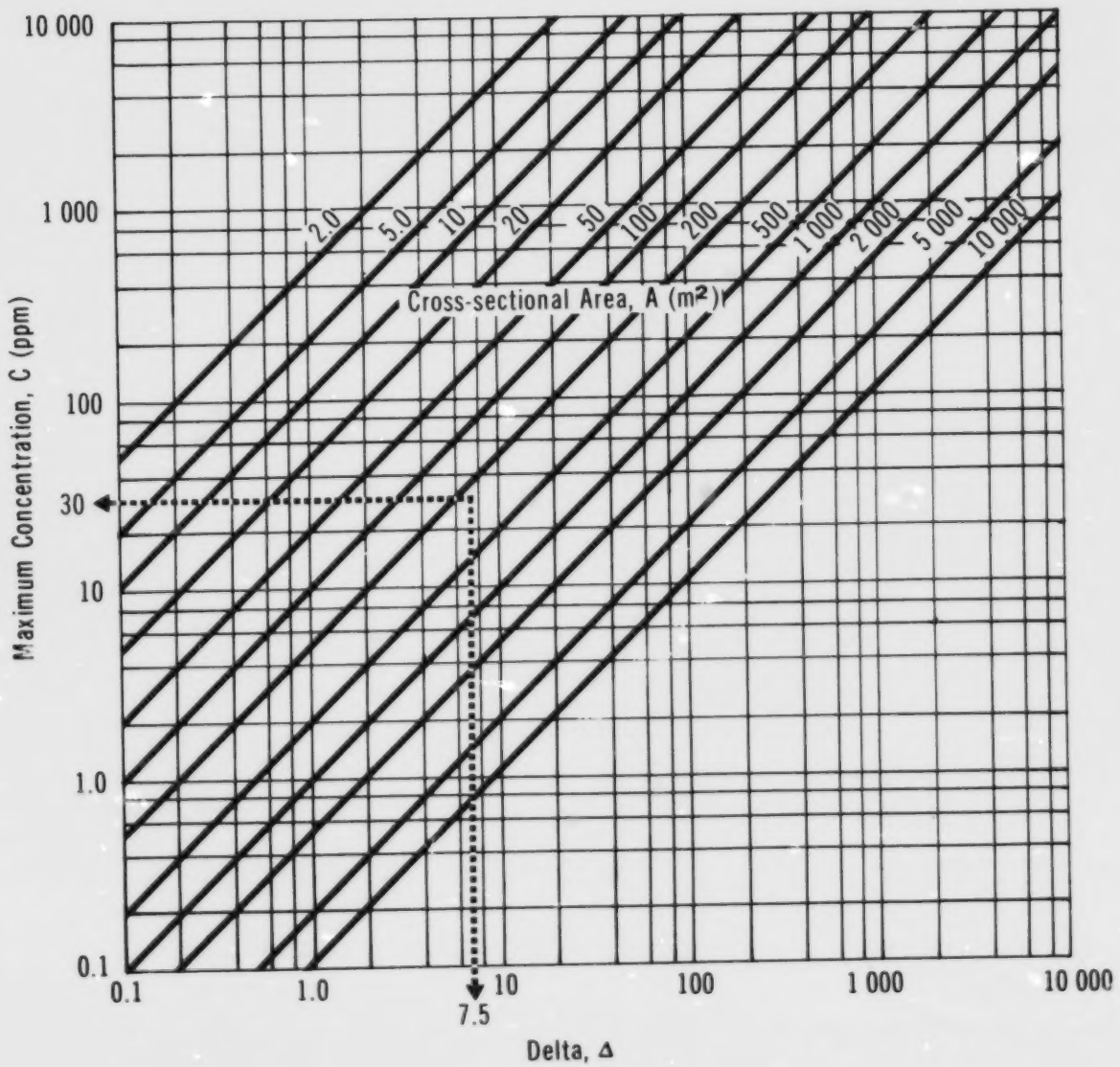


FIGURE 18

PHOSPHORIC ACID

VOLUME vs RADIUS

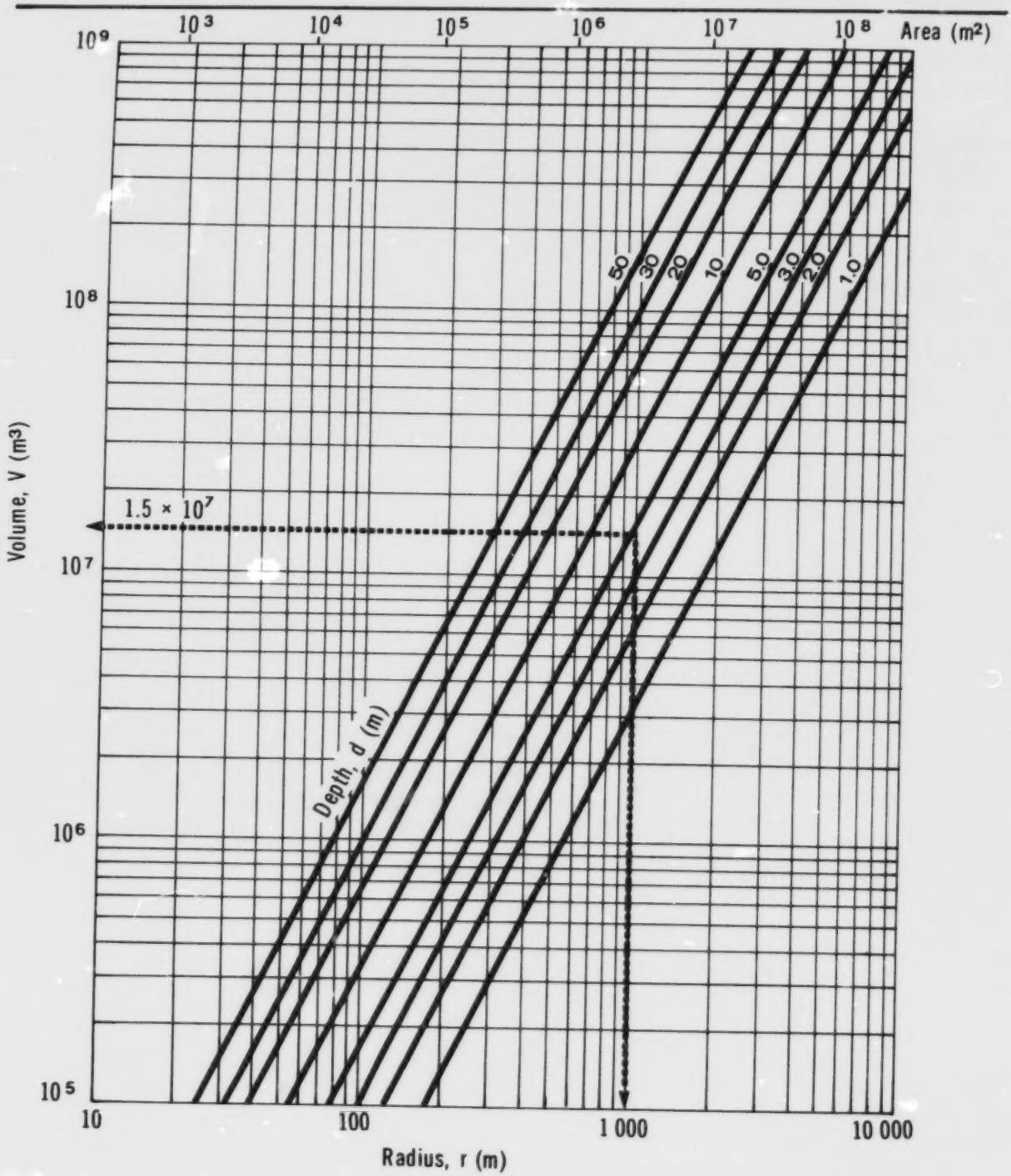
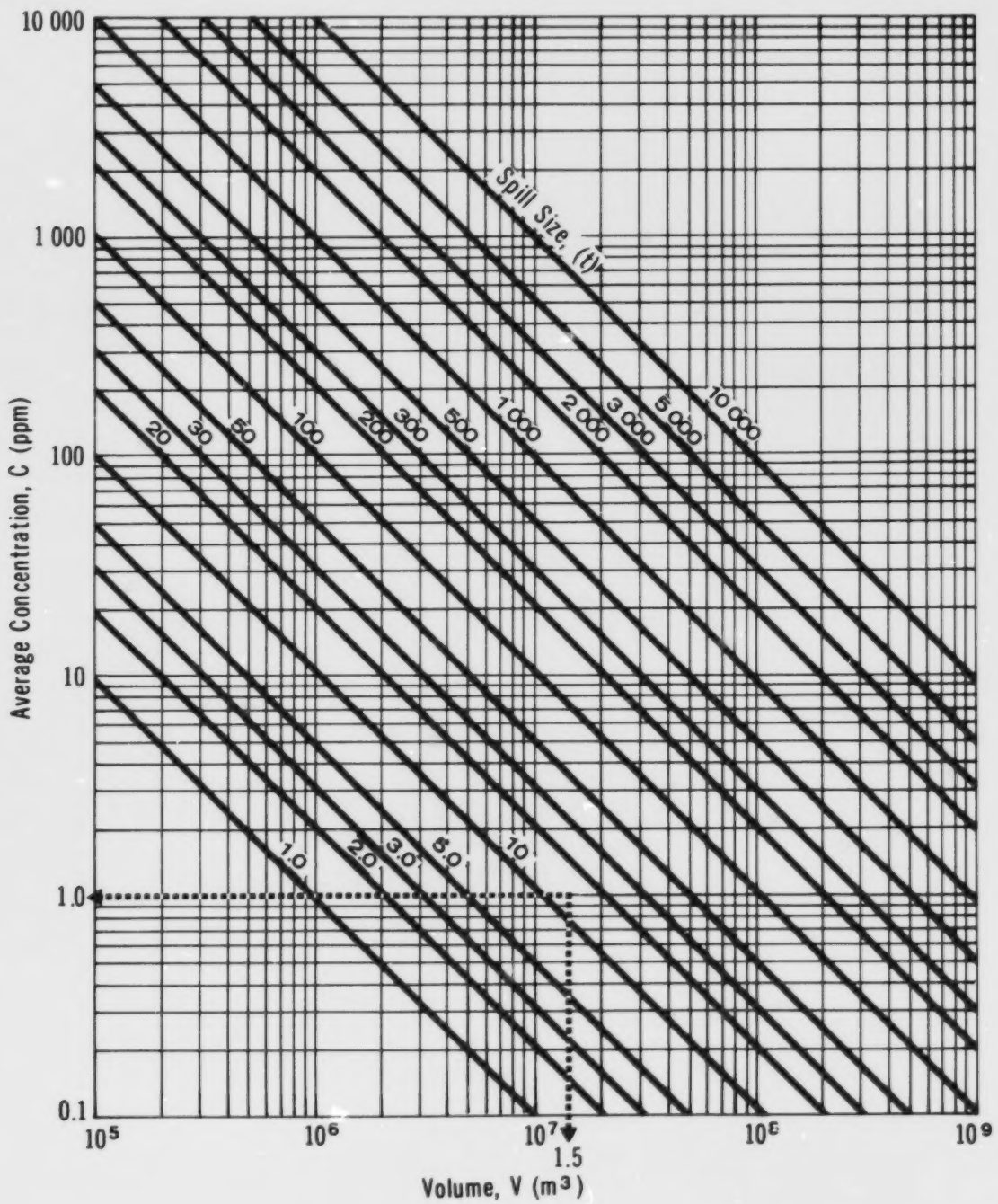


FIGURE 19

PHOSPHORIC ACID

AVERAGE CONCENTRATION vs VOLUME



the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 20 tonne spill of 75 percent phosphoric acid solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- spill mass = 20 tonnes of 75 percent phosphoric acid solution, equivalent to 15 tonnes of phosphoric acid

Step 2: Calculate the time to reach the point of interest

- Use Figure 12
- With X = 5000 m and U = 1 m/s, t = 83 min

Step 3: Calculate the hydraulic radius (r)

- Use Figure 13
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 14
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 15
- With E = 69 m^2/s and t = 83 min, (α) = 2000

Step 6: Calculate delta (Δ)

- Use Figure 16
- With alpha (α) = 2000 and spill mass = 15 tonnes, delta (Δ) = 7.5

Step 7: Compute the stream cross-sectional area (A)

- A = W x d = 50 x 5 = 250 m^2

Step 8: Calculate the maximum concentration (C) at the point of interest

- Use Figure 17
- With Δ = 7.5 and A = 250 m^2, C = 30 ppm

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of 75 percent phosphoric acid solution has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1000 m
- spill mass = 15 tonnes (equivalent weight of phosphoric acid)

Step 2: Determine the volume of water available for dilution

- Use Figure 18
- With r = 1000 m, d = 5 m, the volume is approximately 1.5×10^7 m^3

Step 3: Determine the average concentration

- Use Figure 19
- With V = 1.5×10^7 m^3 and spill mass = 15 tonnes, the average concentration is 1 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of phosphoric acid onto soil and its transport downward through the soil are presented here.

Phosphoric acid is generally shipped in concentrations ranging from 75 to 85 percent by weight in water. When spilled onto soil, it will infiltrate downward, the rate being greater with lower concentrations because of reduced viscosity. Phosphoric acid mixes readily with water. Thus, dilution of the acid will take place if precipitation occurs at the time of the spill or if water is used to flush the site after the spill. If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off or remain ponded.

For this work, the soils have been assumed to be at field capacity (the maximum amount of water the soil can hold after the excess is drained). This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

During transport through the soil, phosphoric acid will dissolve some of the soil material, in particular carbonate-based materials. The acid will be neutralized to some degree, with adsorption of the proton and phosphate ions also possible. However, significant amounts of acid will remain for transport down toward the groundwater table. The analysis used here neglects these retarding factors.

Upon reaching the groundwater table, the acid will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with dilution and dispersion serving to reduce the acid concentration. This is shown schematically in Figure 20.

5.5.2 Equations Describing Phosphoric Acid Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Phosphoric Acid in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

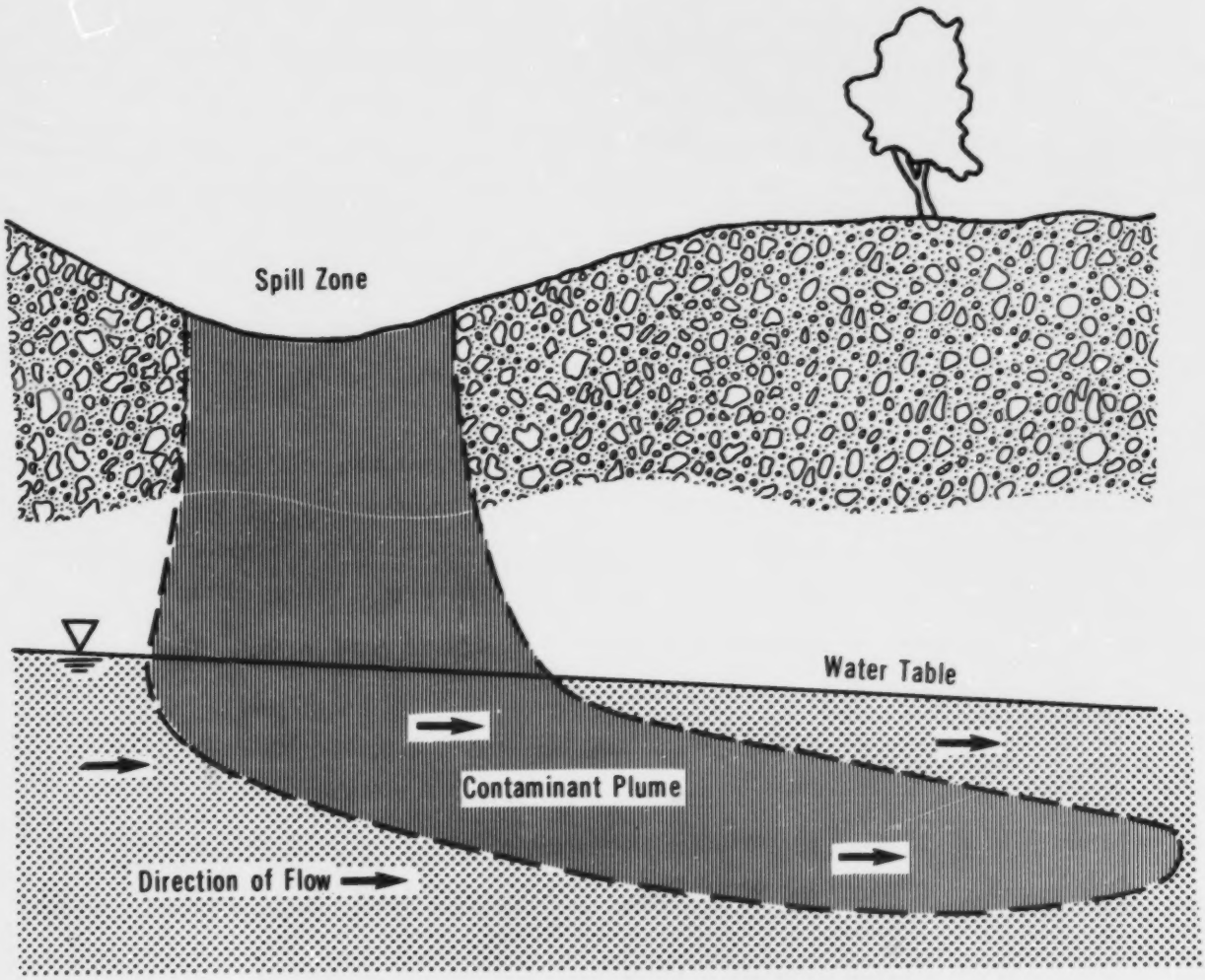
where:
- k = intrinsic permeability of the soil (m^2)
- ρ = mass density of the fluid (kg/m^3)
- μ = absolute viscosity of the fluid ($Pa \cdot s$)
- g = acceleration due to gravity = 9.81 m/s^2

The fluids involved are 75 and 19.6 percent by weight phosphoric acid, and water. The water calculations represent the extreme as phosphoric acid is diluted. The appropriate properties of phosphoric acid are given in the following chart.

FIGURE 20

PHOSPHORIC ACID

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

Property	Phosphoric Acid			Water
	75% by Wt.	19.6% by Wt.		
	20°C	20°C	4°C	20°C
Mass density (ρ), kg/m^3	1579	1113	1120	998
Absolute viscosity (μ), Pa•s	3.7x10-3	1.7x10-3	1.4x10-3	1.0x10-3
Saturated hydraulic conductivity (K_o), m/s	(0.42x10^7)k	(0.63x10^7)k	(0.79x10^7)k	(0.98x10^7)k

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

Property	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n) m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10-9	10-12	10-15
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of phosphoric acid into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p.

A flowchart for the use of the nomograms is presented in Figure 21. The nomograms are presented as Figures 22, 23, and 24. The water line on the nomograms represents the maximum penetration of water at 20°C in time t_p. It is a limiting condition as phosphoric acid becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of 75 percent phosphoric acid has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 32 minutes after the spill.

FIGURE 21

PHOSPHORIC ACID

FLOWCHART FOR NOMOGRAM USE

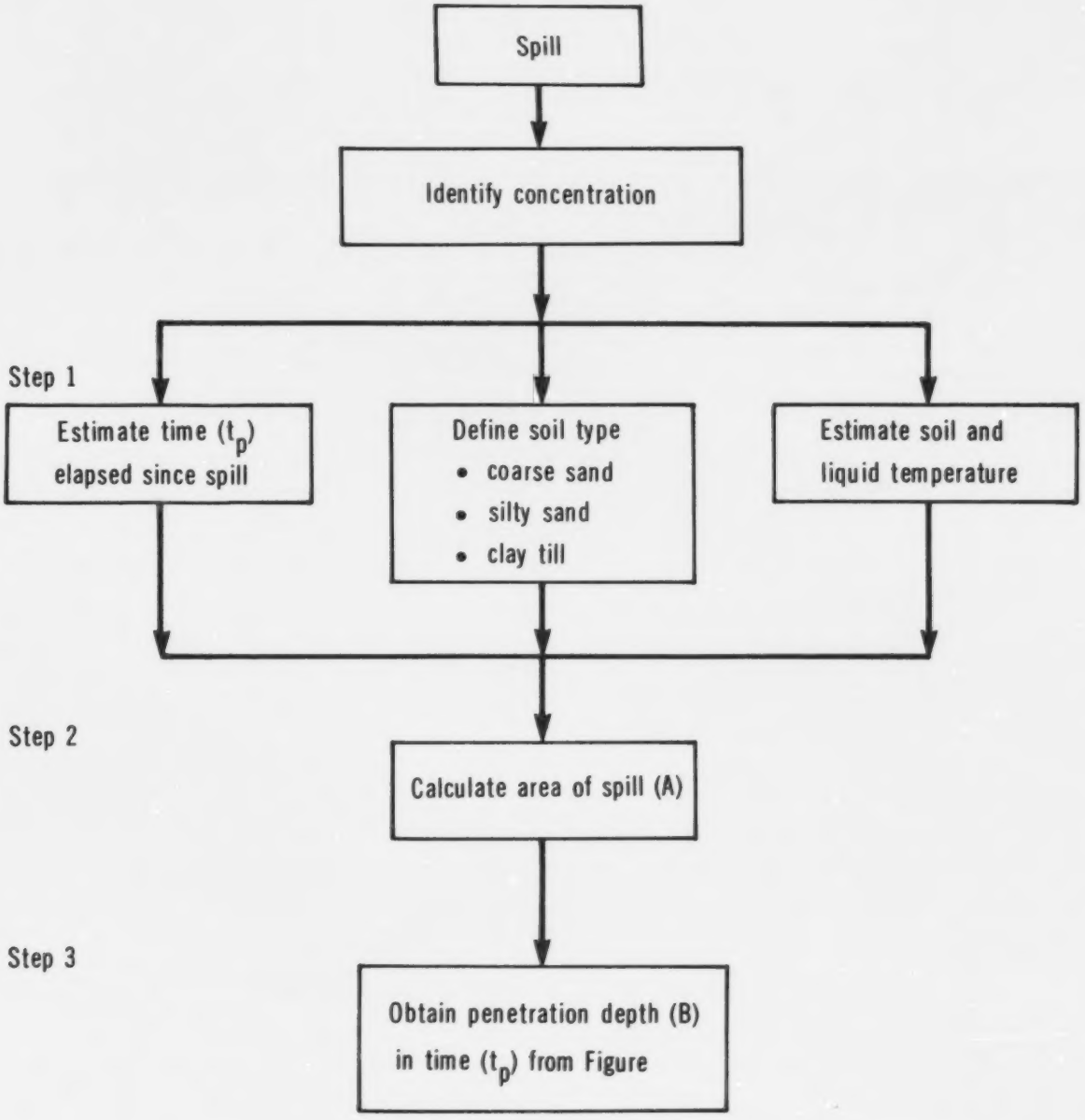


FIGURE 22

PHOSPHORIC ACID

PENETRATION IN COARSE SAND

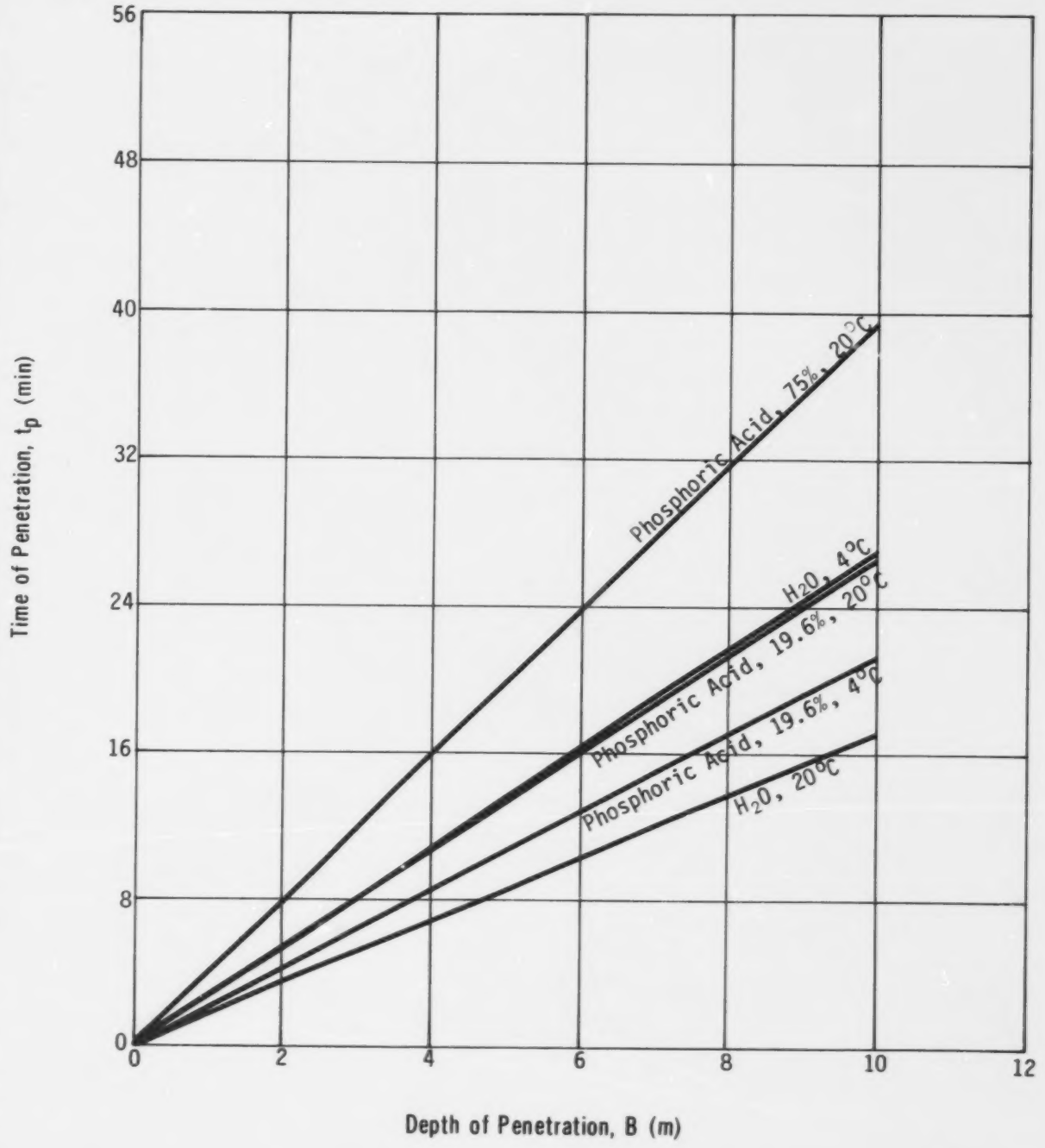


FIGURE 23

PHOSPHORIC ACID

PENETRATION IN SILTY SAND

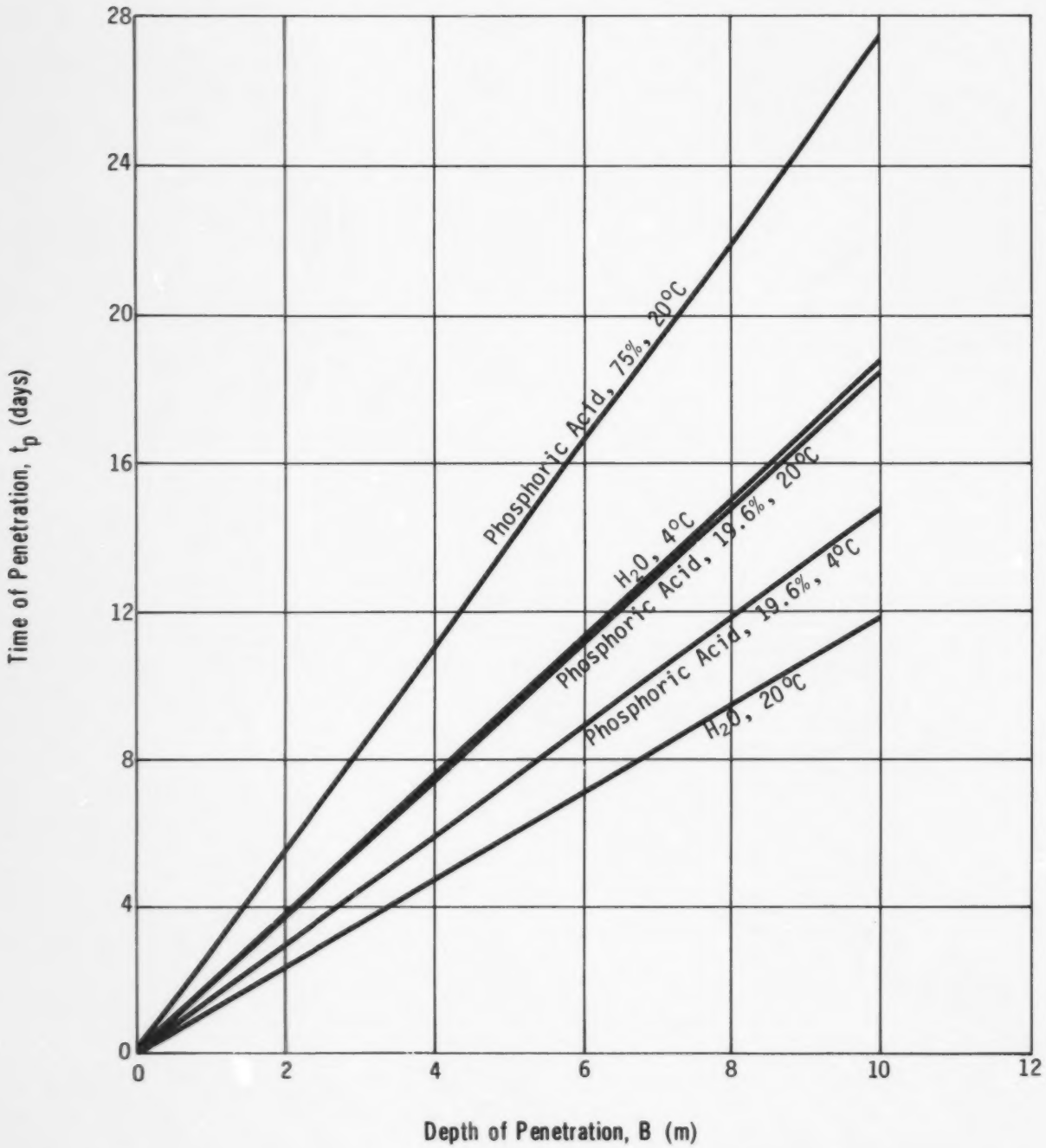
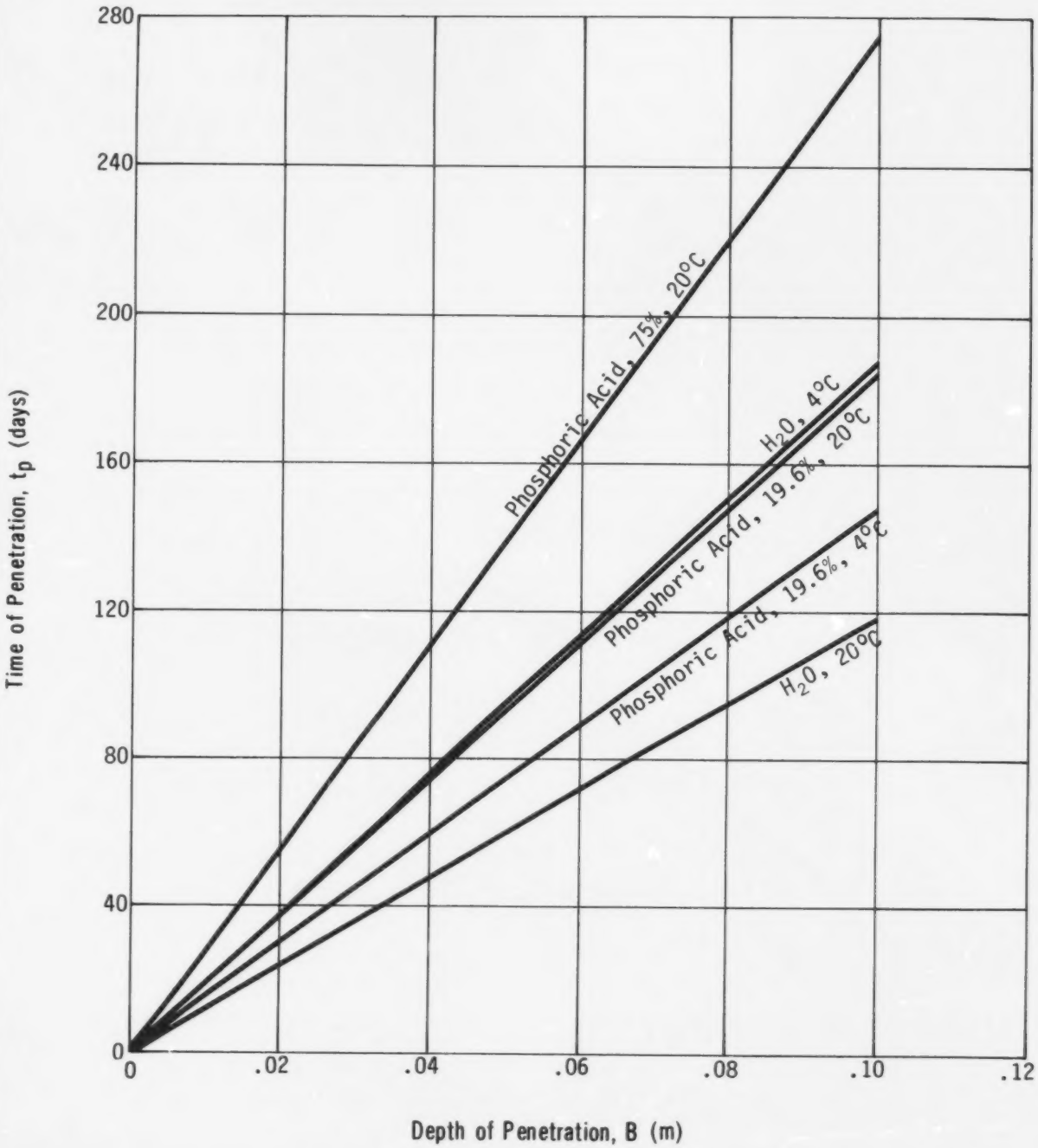


FIGURE 24

PHOSPHORIC ACID

PENETRATION IN CLAY TILL



Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- T = 20°C
- r = 8.6 m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 32 min

Step 2: Calculate the area of the spill

- $A = \pi r^2 = 232\ m^2$

Step 3: Estimate the depth of penetration (B) at time (t_p)

- For coarse sand, B = 8.1 m at t_p = 32 min
- Groundwater table has not been reached in this time

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Drinking Water. Ontario's objective for total phosphorus to avoid nuisance algal concentrations is 10 µg/L (0.01 mg/L) as phosphorus in ice-free months (Water Management Goals 1978).

6.1.2 Air. The Ontario environmental limit for phosphoric acid is 100 $\mu g/m^3$, expressed as P_2O_5 (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Phosphoric acid has been assigned a TL_m96 of 100 to 1000 ppm (RTECS 1979).

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
0.01 (as hydrogen ion)		Stickleback	lethal	pH 5	WQC 1963
0.08	8	Stickleback	lethal	pH 4.0, distilled	WQC 1963
0.2	15 to 57 min	Stickleback	lethal	pH 2.2 to 3.4	WQC 1963
Fish Toxicity Tests					
138	24	Mosquito fish	TL_m	22 to 24°C, turbid	WQC 1963
138	48	Mosquito fish	TL_m	22 to 24°C, turbid	WQC 1963
138	96	Mosquito fish	TL_m	22 to 24°C, turbid	WQC 1963

Microorganisms

Phosphates are nutrients for aquatic life and can stimulate increased growth. A concentration of 0.01 mg/L or less of inorganic phosphorus is recommended to avoid undesirable algal growths (WQC 1963).

6.3 Other Land and Air Toxicity

Plant foliage (peas, beans, beets, rape, and weeds were tested) is destroyed by spraying with 15 to 20 percent phosphoric acid (Takala 1978).

6.4 Degradation

While acidity may be reduced readily by natural water hardness minerals, the phosphate may persist indefinitely (OHM-TADS 1981).

6.5 Long-term Fate and Effects

Abundant phosphate will increase algal blooms and possible eutrophication. Toxic effects of phosphoric acid are largely due to acidity (WQC 1963). Phosphoric acid is not bioaccumulative or bioconcentrative.

7 HUMAN HEALTH

Relatively little information is available on the inhalation toxicity of phosphoric acid despite its wide industrial use. This may be due to the fact that it has a low vapour pressure at room temperature and consequently its effects are generally only seen when it is introduced into the atmosphere as a spray or mist (NIOSH/OSHA 1981). Phosphoric acid is, however, corrosive to most tissues on contact.

No recent toxicological reviews or monographs pertaining to phosphoric acid were encountered in the literature. The TLV® was established by analogy from sulphuric acid. According to the AIHA Hygiene Guide, phosphoric acid is less hazardous than nitric or sulphuric acids (Doc. TLV 1981). No information concerning potential mutagenic, carcinogenic or teratogenic effects of exposure to phosphoric acid was found in the literature. Phosphoric acid is listed in the EPA TSCA Inventory. The compound requires a "corrosive" label in Canada (RTECS 1979).

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. Only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for phosphoric acid are based upon an analogy with the harmful effects of sulphuric acid and the information that phosphoric acid is less hazardous than sulphuric acid (Doc. TLV 1981). Canadian provincial guidelines generally are similar to those of the USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV® (8 h)	USA-ACGIH	1 mg/m^3	TLV 1983
PEL (8 h)	USA-OSHA	1 mg/m^3	NIOSH/OSHA 1981
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	3 mg/m^3	TLV 1983

Guideline (Time)	Origin	Recommended Level	Reference
Other Human Toxicities			
TC_{LO}		100 mg/m^3 (Irritation)	ITII 1981
LD_{LO}		200 mg/kg	RTECS 1979

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Solid phosphoric acid or its solutions may cause skin burns. The solid is especially irritating to skin in the presence of moisture. A 75 percent solution will cause severe skin burns.	NIOSH/OSHA 1981
SPECIES: Rabbit		
2740 mg/kg	LD_{50}	Sax 1984
595 mg (24 h)	Severe irritation.	RTECS 1979

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Conjunctivitis	ITII 1981
Unspecified	Contact may produce irritation and burns.	NIOSH/OSHA 1981
Unspecified	A dilute solution buffered to pH 2.5 caused moderate brief stinging but no injury when dropped in the human eye.	NIOSH/OSHA 1981
SPECIES: Rabbit		
119 mg	Severe irritation.	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour. Phosphoric acid is odourless (Doc. TLV 1981).

7.3.2 Taste. No data.

7.4 Toxicity Studies

7.4.1 Inhalation (of H_3PO_4 mist or P_2O_5).

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
100 mg/m^3	TC_{LO}, Irritation	RTECS 1979
100 mg/m^3	Unendurable except to acclimatized workers. Exposure was to fumes of phosphorus pentoxide, the anhydrous form of phosphoric acid.	Doc. TLV 1981
3.6 to 11.3 mg/m^3	Caused coughing among the unaclimatized, but could be tolerated.	Doc. TLV 1981
0.8 to 5.4 mg/m^3	Concentrations were noticeable but not uncomfortable.	Doc. TLV 1981
Chronic Exposures		
SPECIES: Human		
Unspecified	35 workers employed in a plant producing H_3PO_4 were checked by means of a questionnaire for chronic bronchitis and emphysema. Results showed 45.7 percent with chronic bronchitis, 37.1 percent with obstructive spirometric impairment. These findings were related significantly to the length of work activity as well as to dust and exposure to gaseous fluorides.	Fabbri et al. 1977. IN TDB (on-line) 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Rat		
1530 mg/kg	LD_{50}	RTECS 1979

7.4.3 Skin (systemic effects).

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Rabbit		
2740 mg/kg	LD_{50}	RTECS 1979

7.4.4 Mutagenicity, Teratogenicity and Carcinogenicity. No data.

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation (of acid mist or aerosol).

1. Irritation of the eyes, nose and throat.
2. Coughing.
3. May exacerbate symptoms in workers with obstructive airway disease (NIOSH/OSHA 1981).

7.5.2 Ingestion.

1. Stomach ache.
2. Nausea.
3. Vomiting.
4. Diarrhea (bloody).

5. Burns on mouth and lips.
6. Acidemia (CHRIS 1978).
7. Difficulty breathing.
8. Convulsions.
9. Collapse.
10. Shock.
11. Death.

7.5.3 Skin Contact.

1. Irritation.
2. Burns.

7.5.4 Eye Contact.

1. Irritation.
2. Conjunctivitis (ITII 1981).
3. Eye burns.

7.6 Human Toxicity to Decay or Combustion Products

Phosphoric acid is dangerous when heated to decomposition: toxic fumes of oxides of phosphorus are emitted (Sax 1979).

7.6.1 Phosphorus Pentoxide. Phosphorus pentoxide is corrosive and irritating to mucous surfaces, eyes and skin. The resulting phosphoric acid is less harmful than sulphuric acid. There is no TLV® for this compound. The hygienic standard recommended in the AIHA Guide is 1 mg P_2O_5/m^3 (Patty 1981).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Phosphoric Acid with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Fire					•	•							Not combustible. Upon decomposition, will emit phosphorus oxides	Sax 1979; NFPA 1978
Heat					•	•							When heated to decomposition, emits phosphorus oxides	Sax 1979
CHEMICAL GROUPS														
Alcohols and Glycols	•													EPA 600/2-80-076
Aldehydes	•			•									Polymerization may occur readily	EPA 600/2-80-076
Alkali and Alkaline Earth Metals	•	•		•						•			Hydrogen gas will be formed	EPA 600/2-80-076
Amides	•													EPA 600/2-80-076
Amines	•													EPA 600/2-80-076

8.1 Compatibility of Phosphoric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Azo Compounds	•			•	•								Depending on the azo compound, decomposition or polymerization may occur	EPA 600/2-80-076
Carbamates	•						•							EPA 600/2-80-076
Caustics	•	•								•			Fire may result if the caustic substance is an alkoxide	EPA 600/2-80-076
Combustible Materials	•				•								Possibly some toxic gas formation	EPA 600/2-80-076
Cyanides			•			•							Hydrogen cyanide gas is produced	EPA 600/2-80-076
Dithiocarbamates			•			•							Carbon disulphide gas is produced	EPA 600/2-80-076
Epoxides	•			•									Polymerization will occur	EPA 600/2-80-076
Esters	•				•									EPA 600/2-80-076
Explosives	•		•											EPA 600/2-80-076

8.1 Compatibility of Phosphoric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Fluorides						•							Toxic and corrosive hydrogen fluoride gas is produced	EPA 600/2-80-076
Halogenated Organics	•				•	•							Toxic fumes of hydrogen halides may be formed	EPA 600/2-80-076
Isocyanates					•									EPA 600/2-80-076
Ketones	•													EPA 600/2-80-076
Mercaptans			•		•	•							Decomposition may also occur	EPA 600/2-80-076
Metal Powders, Vapours or Sponges	•		•	•						•			Hydrogen gas will be formed	EPA 600/2-80-076
Metal Sheets, Rods Drops	•	•		•									Hydrogen gas will be formed	EPA 600/2-80-076
Nitrides	•			•		•							Ammonia gas may be evolved	EPA 600/2-80-076
Nitriles	•			•		•							Exothermic reaction releasing hydrogen cyanide gas	EPA 600/2-80-076

8.1 Compatibility of Phosphoric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Organic Peroxides	•		•			•							Explosive decomposition will occur. Oxygen can also be generated	EPA 600/2-80-076
Organophosphates	•					•							Possibly some toxic gas formation	EPA 600/2-80-076
Phenols and Cresols	•					•								EPA 600/2-80-076
Polymerizable Compounds				•									Polymerization may occur	EPA 600/2-80-076
Strong Oxidizing Agents	•					•	•			•			Halogen gases may be formed	EPA 600/2-80-076
Strong Reducing Agents	•	•		•			•						Hydrogen gas may ignite spontaneously. Metal phosphides and inorganic sulphides may evolve extremely toxic and flammable fumes	EPA 600/2-80-076
Sulphides				•			•						Hydrogen sulphide gas is produced	EPA 600/2-

8.1 Compatibility of Phosphoric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Toxic Metals									•				e.g., As, Pb	EPA 600/2-80-076
Unsaturated Halides	•												Exothermic acid catalyzed hydration	EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Phosphoric acid is a noncombustible liquid; however, contact with some metals may produce hydrogen gas which forms flammable mixtures with air (NFPA 1978). Heating phosphoric acid to decomposition produces phosphorus pentoxide (Hooker MSDS 1976). Containers may also explode in heat of fire (ERG 1980).

9.1.2 Fire Extinguishing Agents. Phosphoric acid is not combustible. Most agents are compatible with phosphoric acid; however, if a fire is involved, choose extinguishing agents on the basis of other materials present.

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Avoid skin contact and inhalation (GE 1977).

9.1.3.2 Spills on land. For small spills, cover the contaminated area with sodium bicarbonate or with a mixture of soda ash/slaked lime. Mix and add water if necessary to form a slurry. Scoop up slurry for disposal and wash site with soda ash solution (Ashland MSDS 1980).

For large spills, contain if possible by forming mechanical barrier and/or chemical barriers to prevent spreading. Neutralize spilled acid with an alkaline material such as soda ash or lime. Lime is the preferred treating agent because of the low solubility of the calcium phosphate formed.

9.1.3.3 Spills in water. Contain if possible. Neutralize with lime or sodium bicarbonate (EPA 670/2-75-042). Calcium carbonate and soda ash may also be considered as neutralizing agents (CG-D-38-76).

9.1.4 Cleanup and Treatment.

9.1.4.1 General. For treatment of contaminated water, precipitation with lime followed by gravity separation of solids and final neutralization of residual alkali with hydrochloric acid is recommended. During precipitation, an anionic polymer may be added to assist in settling of the solids. If necessary, the water, after treatment with lime, can pass through dual-media filtration to remove the solids and then be neutralized with hydrochloric acid prior to discharge (EPA 600/2-77-227). Removal of phosphoric acid from waste water can also be accomplished with Dowex SBR-P resin (an ion exchange resin) which will remove at least 75 percent of the material and can be back-flushed with water to remove the acid (Laney 1975).

9.1.5 Disposal. Waste phosphoric acid must never be discharged directly into sewers or surface waters. Following neutralization, either at the spill site or at a waste management facility, the resultant sludge can be disposed of to a secure landfill. Phosphoric acid neutralized with lime can be used as a fertilizer.

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be phosphoric acid:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent any possibility of repeated or prolonged skin contact with solid or liquid phosphoric acid (NIOSH/OSHA 1981).
- Dust- and splash-proof safety goggles are recommended where there is any possibility of solid or liquid phosphoric acid or solutions containing phosphoric acid contacting the eyes (NIOSH/OSHA 1981). Chemical safety goggles should also be considered (GE 1977).
- Rubber is recommended for gloves, boots and aprons (GE 1977).
- The following clothing materials show breakthrough times of approximately 1 hour (Little 1983):

Acid Concentration	Material
<30%	Butyl rubber, natural rubber, chlorinated polyethylene, polyvinyl chloride and Viton
30 - 70%	Viton and neoprene
>70%	Butyl rubber, neoprene, chlorinated polyethylene, polyvinyl chloride, and Viton

- The following chemical suit materials are recommended for protection against phosphoric acid (EE-20): butyl, cloropel, PVC (excellent resistance) and neoprene (good resistance).
- Eye wash stations and chemical safety showers should be readily available in areas of use and spill situations (GE 1977).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where phosphoric acid is present (NIOSH/OSHA 1978).

Condition	Minimum Respiratory Protection* Required Above 1 mg/m^3
Particulate or Vapour Concentration (Mist)	
50 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
2000 mg/m^3 or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.

Condition	Minimum Respiratory Protection* Required Above 1 mg/m^3
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

* Only NIOSH-approved or MSHA-approved equipment should be used.

9.1.7 Storage Precautions. Store 85 percent acid above 21°C, 80 percent acid above 4°C, and 75 percent acid above -18°C to prevent crystallization (phosphoric acid solutions will normally supercool without crystallization, but this effect is unpredictable). Phosphoric acids should be stored in clean, ventilated storage areas with good drainage. The acid should be stored away from reactive materials, metal powders, etc. Soda ash or lime should be kept in the same general areas for emergency use. Corrosion of equipment and surfaces should be considered in areas where hot or "misted" phosphoric acid is present (GE 1977).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study.

Pumps for Liquids	U.S Coast Guard ADAPTS
Treating Agents	Hazorb (sorbent)

10 PREVIOUS SPILL EXPERIENCE

10.1 General

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequence of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.2 Train Derailment (HMIR 1981)

In a train derailment near an urban area, one of the five derailed tank cars was punctured and spilled approximately 114 000 L of phosphoric acid. Response personnel arrived at the spill site and contained the spilled product. The collected acid was then removed to a local landfill site, where it was dumped in a pit lined with lime. More lime was added until the mixture solidified. The mixture was subsequently spread over a nearby field as fertilizer.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows:

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found; they have been presented as well.

11.1 Quantitative Method for the Detection of Phosphoric Acid in Air

11.1.1 Colourimetric (NIOSH 1977). A range of 0.47 to 1.93 mg/m^3 (0.12-0.48 ppm) of phosphoric acid (as a mist or an aerosol) in air may be determined colourimetrically.

A known volume of air is drawn through a 37 mm, 0.8 µm pore size cellulose-ester filter housed in a 3-piece cassette filter holder. A sample size of 90 L at a flow rate of 1.5 L/min is recommended.

The filter sample is transferred to a 125 mL beaker using a pair of tweezers. A 10 mL volume of water is added and the beaker covered with a watchglass, then placed on a steam bath for 10 min. The liquid is decanted from the beaker into a 50 mL volumetric flask and the procedure repeated with another 10 mL volume of water. The inside of the beaker is rinsed with an additional 5 mL of water and the rinsing added to the flask.

A 5 mL volume of sodium molybdate solution is added to the flask. It is prepared by dissolving 25.0 g of sodium molybdate dihydrate in 1 L of 10 N sulphuric acid. A 2 mL volume of hydrazine sulphate is also added to the volumetric flask. It is prepared by dissolving 1.5 g of hydrazine sulphate in 1 L of distilled water.

The contents of the volumetric flask are mixed and diluted to 50 mL. The flask is immersed in a boiling waterbath for 10 min, removed, and rapidly cooled to room temperature.

The absorbance is determined at 830 nm on a suitable spectrophotometer using matched 1 cm cells against a reagent blank. The phosphoric acid is determined quantitatively using a calibration curve.

11.2 Qualitative Method for the Detection of Phosphoric Acid in Air

The sample is collected and extracted as in Section 11.1.1. A 1 mL aliquot of the decant from the first or second 10 mL portion is placed in a beaker. A 5 mL volume of concentrated nitric acid is added and the mixture evaporated to 1 mL in a fume hood. A 2 mL volume of water is added and the mixture transferred to a test tube. A 1 mL volume of 1 M ammonium nitrate and 2 mL of 0.5 M ammonium molybdate are added. The solution is heated to boiling. The formation of a yellow precipitate of ammonium phosphomolybdate indicates phospate (Welcher 1955).

11.3 Quantitative Method for the Detection of Phosphoric Acid in Water

11.3.1 Colourimetric (AWWA 1981). A range of 1 to 20 mg/L (ppm) of phosphoric acid as phosphate may be determined colourimetrically.

A minimum of 1 L of respresentative sample is collected in a glass container which has been washed with dilute hydrochloric acid. If the sample pH is less than 4, a 50 mL aliquot of sample is diluted to 150 mL in a volumetric flask with distilled water. If the sample is excessively coloured, a 50 mL volume is shaken with 200 g activated carbon for 5 min then filtered using Whatman 42 filter paper to remove the carbon.

A 35 mL aliquot or less of sample is placed in a 50 mL volumetric flask. A 10 mL volume of vanadate-molybdate reagent is added and the volume taken to mark with distilled water. The vanadate-molydbate reagent is prepared in two stages. The molybdate solution is prepared by dissolving 25 g ammonium molybdate tetrahydrate in 300 mL distilled water. The vanadate solution is prepared by dissolving 1.25 g ammonium metavanadate, by heating to boiling in 300 mL distilled water. The mixture is cooled and 330 mL of concentrated hydrochloric acid are added. The mixture is allowed to cool, then combined with the molybdate solution and the total volume taken to 1 L.

The treated sample is left to develop for 10 min; the absorbance is then determined at 400 nm using a suitable spectrophotometer with matched 1 cm cells. A blank determination must also be made. The phosphate is determined using a calibration curve.

11.4 Qualitative Method for the Detection of Phosphoric Acid in Water

The sample is collected as in Section 11.3.1. A 1 mL aliquot of sample is placed in a beaker. A 5 mL volume of concentrated nitric acid is added and the mixture evaporated to 1 mL in a fume hood. A 2 mL volume of water is added and the mixture transferred to a test tube. A 1 mL volume of 1 M ammonium nitrate and 2 mL of 0.5 M ammonium molybdate are added. The solution is heated to boiling. The formation of a yellow precipitate of ammonium phosphomolybdate indicates phosphate (Welcher 1955).

11.5 Quantitative Method for the Detection of Phosphoric Acid in Soil

11.5.1 Colourimetric (Hesse 1972). A range of 0 to 20 ppm of phosphoric acid as phosphorus may be determined colourimetrically.

A 1.0 g, 0.5 mm (sieve-size), soil sample is placed in a centrifuge tube and mixed with 10 mL of concentrated hydrochloric acid. It is then heated on a steam bath for 10 min and a further 10 mL of concentrated hydrochloric acid are added. The mixture is allowed to stand at room temperature for 60 min, 50 mL of water added, and then centrifuged.

The solution is decanted into a 250 mL volumetric flask and made to volume. A suitable aliquot of solution is transferred to a 50 mL volumetric flask and 5 mL of 60 percent perchloric acid are added. The volume is taken to 30 mL with water and 5 mL of ammonium vanadate solution are added. If a precipitate forms in the sample solution, it is filtered off. The ammonium vanadate solution is prepared by dissolving 2.345 g anhydrous ammonium vanadate in 400 mL hot water, adding 17 mL 60 percent perchloric acid and diluting to 1 L. The sample treatment continues with the addition of 5 mL ammonium molybdate solution to the 50 mL volumetric flask. The ammonium molybdate solution is prepared by dissolving 25 g ammonium molybdate in 400 mL water at 50°C, cooling, and filtering if needed. The volume is taken to 500 mL and the solution stored in a brown glass bottle.

The sample solution is diluted to 50 mL in water. The colour is allowed to develop for 30 min. The absorbance is measured at 470 nm using a suitable spectrophotometer and matched 1 cm cells. A blank determination must also be made. The phosphate is determined using a calibration curve.

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